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— SECTION B —

CHEMICAL SCIENCES

Contents

	Page
A Periodic Arrangement of the Elements—*D. F. Stedman*	199
The Equilibrium Data and Crystallization Characteristics of the System: Picric Acid–Dinitrophenol–Picramide—*A. N. Campbell, E. J. Pritchard, A. J. R. Campbell, and M. L. Boyd*	211
A Study of Systems Involving Trinitrotoluene, RDX, NENO, and Dinitrobenzene, with Particular Reference to the Composition of the Binary Eutectics—*A. N. Campbell and H. A. Kushnarov*	216
A Method of Analysis for the System: Benzene–Ethyl Alcohol–Carbon Tetrachloride—*A. N. Campbell and S. I. Miller*	228
The Chromates of Silver and Copper—*A. N. Campbell and H. P. Lemaire*	243
The Determination of Particle Size by Light Scattering—*J. Bardwell and C. Sivertz*	255
Production and Properties of 2,3-Butanediol. XXI. Catalytic Cracking of Cyclic Acetals and Ketals Derived from 2,3-Butanediol—*A. C. Neish, V. C. Haskell, and F. J. Macdonald*	266
The Reaction of Cyanogen with 1,3-Butadiene—*G. J. Janz, R. G. Ascah, and A. G. Keenan*	272
The Preparation of 2-Cyanopyridines from Cyanogen and Some Simple 1,3-Dienes—*G. J. Janz and A. G. Keenan*	283
The Preparation of Cyanogen Chloride—*H. W. Barnett, R. G. Davis, and R. P. Graham*	289
Dimethyldinitroöxamide—*O. C. W. Allenby and G. F. Wright*	295
Osmotic Pressure Measurement and the Instability of High Polymers—*A. F. Sirianni, L. M. Wise, and R. L. McIntosh*	301
The Polarographic Determination of Tin in High Purity Zinc and Zinc Die-casting Alloys—*R. C. Hawkings, D. Simpson, and H. G. Thode*	322
Concerning the Theoretical Aspects of the Reaction of Cyanogen and 1,3-Butadiene—*G. J. Janz*	331

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A PERIODIC ARRANGEMENT OF THE ELEMENTS[1]

BY D. F. STEDMAN[2]

Abstract

A cyclic spiral arrangement of the elements is discussed. This arrangement is best considered as the vertical projection of a solid model, somewhat conical in form. The planar arrangement is modified from the plan of the solid model only as necessary to clarify the presentation.

Considered chemically this arrangement has the advantage of separating each type of element without ambiguity, and the rare earths and 'VIII groups' are also accommodated as an integral and significant part of the orderly development of the table. The *A* and *B* grouping is also eliminated.

The opposing nature of the electropositive and electronegative elements is clearly shown, and the various broad classes of elements are closely grouped, e.g., the active : inactive metals; elements forming predominantly inorganic groupings : elements readily forming organic compounds; the acid forming elements; the various analytical groups, etc.

The table also requires a minimum of artificial arrangement and utilizes a definite scale in both the planar and solid model.

This proposed arrangement of the elements is best considered as a solid model, views of which are shown in Figs. 1 and 2. The planar form is shown in Fig. 3, fundamentally a plan of the solid form, modified only as necessary to produce satisfactory spacing between the elements.

Three Dimensional Model

This model is based on a fundamentally conical arrangement, hydrogen being at the apex and the series of elements being arranged in a spiral, 4 mm. vertical separation being allowed for each element in the actual model shown in the illustrations.

It is intended to be considered that there are three types of spacings between elements; the spacing of elements through the thickness of the model represents the greatest degree of chemical differences, while lesser degrees of difference are represented by the horizontal distances round the surface of the model, these being shown by the thin 'development' lines connecting successive elements. The vertical direction indicates the general families of elements and is shown in heavy lines.

[1] *Manuscript received June 14, 1946.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1515.

[2] *Chemist.*

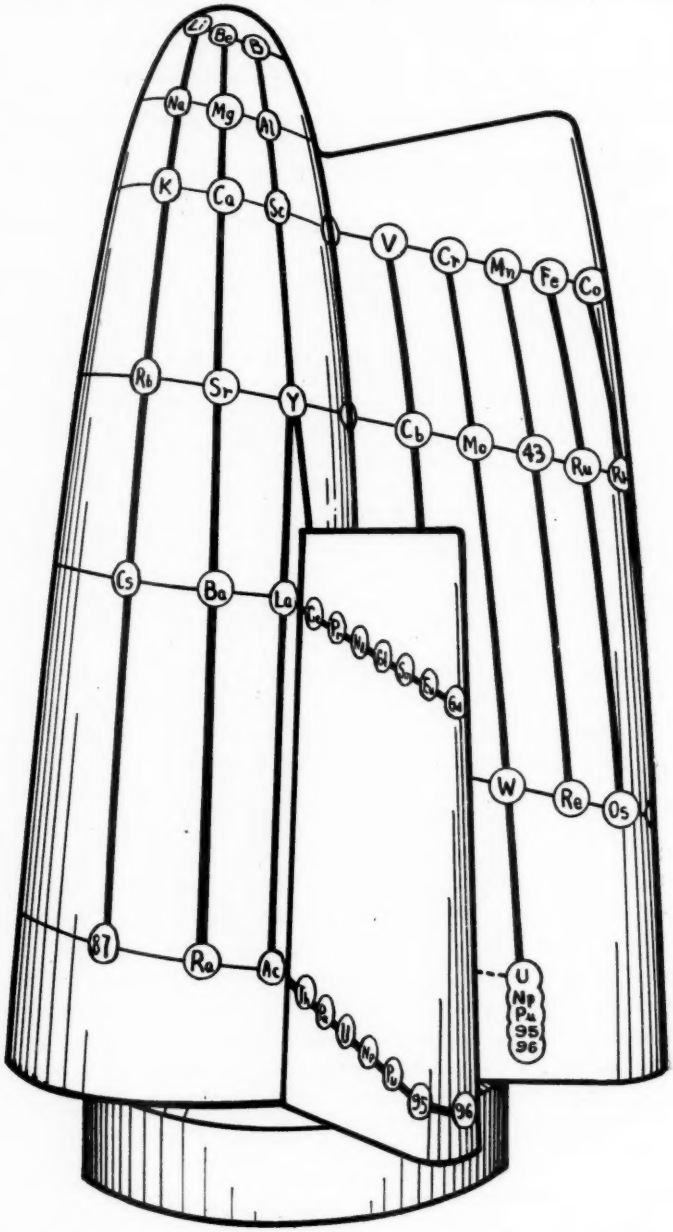

FIG. 1. *Three dimensional model. "Front view". Groups I to VIII.*

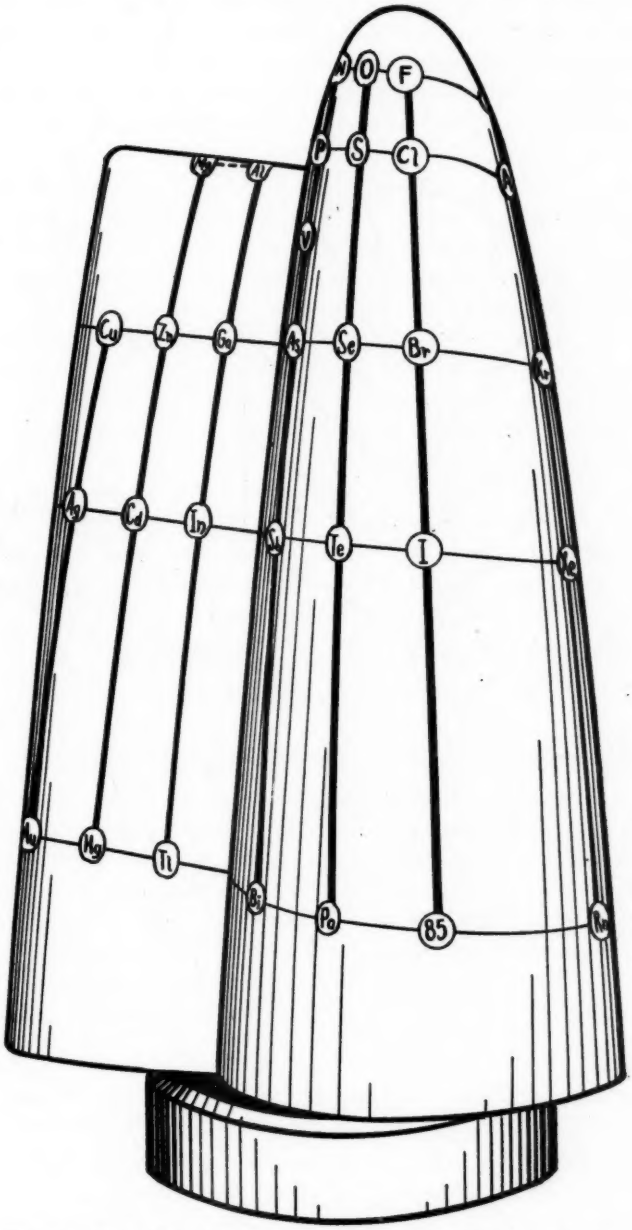

FIG. 2. *Three dimensional model. "Back view". Copper, silver, gold, and electronegative groups.*

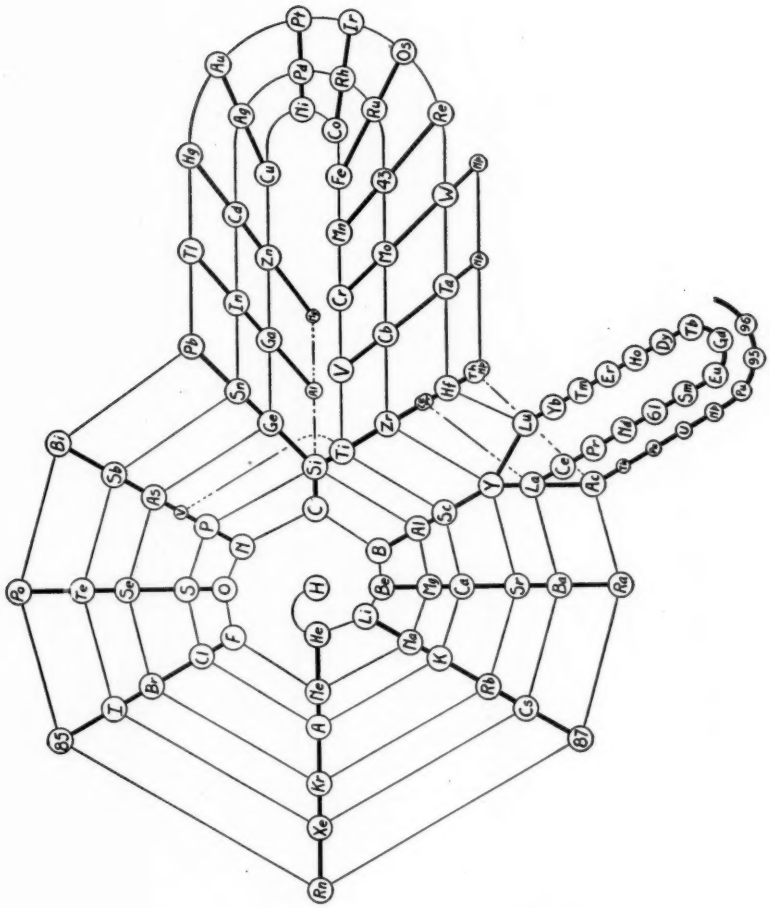

FIG. 3. *Planar diagram.*

It is of course difficult, if not impossible, to maintain a precisely scalar thickness through such a model to indicate all degrees of chemical differences, especially in view of the fact that differences occur not only in degree, but also in type. This model however attempts to indicate the broad classes of variation as nearly as possible by the various directions on or through the model.

The model consists of three parts:—

(*a*) A cubic paraboloid of revolution accommodating the main octet families, typified by all elements up to titanium. This part of the model uses a cubic relation between the thickness and vertical dimension in order to illustrate the great differences between elements on opposite sides of the model by interposing a considerable thickness between them.

(*b*) An 'extension' attached to one side of parabolic section, completed by half of a paraboloid of revolution. The second power relation of thickness to vertical distance and thinner section is used in this part of the model to illustrate that differences although considerable are less than in the main octet groupings, and elements from vanadium to gallium with corresponding families of higher atomic weight are grouped on this section.

(*c*) Another smaller extension, of acute triangular section, is also provided for the rare earth families, the first power relation and very thin section here illustrating the very small differences between opposite elements, and in this region the thin development line is changed to the thick family line for the same reason.

Planar Diagram

This is to be considered as a plan of the solid, but slight changes from direct vertical projection give a more satisfactory presentation. Thus the radial scale from hydrogen in this diagram is proportional to the square root of the atomic number instead of cube root; otherwise the higher atomic numbers are too crowded when reduced to a fairly small diagram. The line from titanium to iron is also drawn parallel to the line from copper to germanium, and similarly with the other development lines in homologous groups. The spacing between these parallel development lines also follows by projection from the initial and final elements, titanium, germanium, etc., as the case may be, rather than by vertical projection from the solid. These scalar changes, or the scales themselves, are of course merely aids in drawing, and are not of actual significance in the arrangement. Apart from such minor changes both diagrams are interchangeable and will be considered together, as the organization and groupings are identical in both.

The planar arrangement is superficially similar to several other spiral arrangements, e.g. that proposed by K.G. Irwin (1), but so far as the author is aware none of these other classifications assist much in illustrating or clarifying the *relations* between the elements, on which the present arrangement is based.

General Groupings in the Arrangement

Main Cubic Paraboloid 'Cone'

It will be seen that this portion of the arrangement follows the types of the first two and a half 'short periods', the eight elements of each cycle being arranged in the planar form as a spiral of radius increasing as the square root of the atomic number, while in the model each successive element is 4 mm. lower than the preceding. The angular distribution of the families is arranged as nearly as may be to illustrate the degree of difference between each family, the greatest spacings being provided in both directions from the zero group.

One of the major features of this arrangement is that only two families are considered as true branched families, instead of seven as in the Mendelejeff system, and of these two, one, at yttrium, is not usually considered in this manner.

Consider the branch at silicon first. The family carbon, silicon, germanium, tin, lead is an excellent and continuous family, especially in relation to their organic compounds, while carbon, silicon, titanium, zirconium, hafnium is almost as closely a related family, especially in relation to their inorganic compounds. In general all elements on the germanium side of the table give organic compounds very readily, while, after crossing the mid-line of the diagram, this property rapidly diminishes.

On considering the process of building up the heavier elements, starting at hydrogen, the first two short periods are quite homologous, but after passing titanium, the next element, vanadium, shows many properties quite different from those of phosphorus, and this is indicated by the branch in the development line, by placing vanadium on the side extension. However, vanadium also shows some properties very much like those of phosphorus, and consequently vanadium is also shown in the phosphorus family, as a smaller circle, indicating that only a part of the properties of vanadium are represented by this small circle. The development line leading to this partial of vanadium is shown dotted.

In this arrangement vanadium is therefore called a transition element, and in this discussion the usual use of this term, e.g., as frequently applied generally to rare earths and often VIII group elements, etc., is abandoned, since these elements have here an orderly and significant position.

Transition elements here considered are therefore those elements which occur immediately following a change in development, and which act partially as if such a change had not occurred.

It might also be noted that the use of small symbols to illustrate the partial nature of such transition elements as vanadium in the phosphorus family is not of course necessary, but is merely offered for consideration.

This transition effect may also be considered as continuing to a very slight extent with both chromium and manganese, but in these cases the similarity to the sulphur and chlorine families respectively is restricted to one class of compound in each case, the chromates and manganates being similar to the

sulphates, and the permanganates being similar to the perchlorates. It seems hardly necessary to indicate such abbreviated similarity in any definite manner in the table.

In further consideration of transition effects at this branch, it is clear in the next turn of the spiral that columbium does not show any perceptible resemblance to arsenic and consequently transition effects are restricted mainly to vanadium at this branch from the main octet families.

Main Side Extension

Elements following vanadium are arranged in loops around this side extension, and rejoin the main octet again on reaching germanium. The iron–cobalt–nickel triad and the heavier homologues are frequently considered as differing from their neighbours, and consequently in many tables all nine elements are grouped together as Group VIII. In the present arrangement it is considered that the whole process from vanadium to nickel is continuous, but that the chemical difference for each step becomes successively less. In order to show this the spacings along this development line decrease continuously from vanadium to nickel.

Following nickel, however, chemical differences again become quite marked, and elements are therefore evenly spaced again from nickel to germanium, the same arrangement being followed for each of the homologous triads.

It might perhaps be noted that although, for instance, manganese and zinc are not very far apart, particularly in the planar form, it is not intended to suggest that they are actually chemically similar. These groups of elements are on opposite sides of the solid model and the thinness of this section is merely intended to express the fact that the difference between elements on opposite sides is here much less than for those on opposite sides of the main octet series.

The development lines in passing round this side extension rejoin the main octet series at germanium, tin, or lead, as the case may be. The major criterion is of course that these elements are again able to complete an inert gas shell by adding electrons equal in number to their maximum valence, and they are therefore again in this respect similar to carbon and silicon. The elements on the titanium to thorium branch, however, cannot complete such a shell by adding any available number of electrons, and in this respect they differ from silicon and therefore represent the start of a change in the development of immediately following elements.

Rare Earth Extension

The above discussed branch in the silicon families, to titanium and germanium respectively, results from the continued addition of peripheral electrons, causing what might be termed overloading and structural weakness in the underlying electronic foundations in the atom. Thus the inner electronic structure is then unable to support more peripheral charge and the addition of further electrons necessarily results in 'stiffening' the inner electronic structure before the external electronic loading can be increased. However,

in the case of the silicon branches the level considered is only one level below the valence electrons, and is still open to chemical attack. Hence the added electrons produce considerable chemical difference for each added electron. Although this is of course all well known, the usual periodic tables do not indicate these processes as clearly as the present arrangement or the abrupt start of these processes at vanadium.

The electronic processes concerned in the structure of the rare earths are quite analogous to the electronic effects resulting in the production of the two silicon families, but in the case of the rare earths the inner electronic weakness is more deep-seated, the added electrons reaching two quantum groups further in the atom. The chemical differences therefore are of course very slight, and in the usual periodic table the rare earths are placed in an appendix of some sort, as peculiar to themselves.

However, this procedure is unnecessary in the present arrangement and the yttrium branch is developed exactly as the silicon branch, which it resembles in many ways, even in detail. Thus silicon shows greater resemblance to germanium than it does to the closer titanium, while yttrium similarly shows greater resemblance to lutecium than to lanthanum.

In this rare earth group it will be seen that immediately following the change in development at lanthanum, cerium and praseodymium show transition effects exactly analogous to the effects noted with vanadium, and appear also as IV state in the zirconium family.

The next cycle of elements starting from actinium, of still heavier elements round the rare earth loop, are not usually considered as rare earth members and although the author drew this table in this manner 16 years ago (up to uranium of course) the evidence was then rather scanty. Until recently the major evidence suggesting this arrangement was:—

1. Primary rare earth minerals are never found without either thorium or uranium.

2. Primary thorium and uranium minerals are never found without rare earths.

3. Uranium is not associated with tungsten in minerals.

4. Although thorium shows exclusive tetravalence, this does not necessarily suggest that the rare earth development is abandoned in the actinium cycle. The tetravalence of thorium in fact might be expected to be strongly developed, as cerium shows definite transition to IV state, and the larger ionic diameter of thorium and its more metallic nature would suggest that this transition would in any case be much more marked than with cerium. It might be noted in passing that the effects discussed in comparing thorium with cerium are exactly the opposite of those noted in comparing columbium with vanadium, as related to transition effects. In the next heavier cycle following vanadium the *more* metallic nature of columbium greatly *reduces* the probability of transition effects and in fact with columbium no transition is detected,

although columbium with respect to the silicon families is in a position quite comparable with that of thorium with respect to the yttrium families.

5. The fusion point of uranium element is much too low for any close relation with tungsten and all its neighbours.

6. Chromium, molybdenum, and tungsten are also fairly easily reduced and also increasingly inert, while uranium differs very greatly in both properties.

7. Furthermore, tungsten is not a good 'carrier' for uranium, i.e., they are rather easily separated in many reactions.

8. The absorption spectrum of uranium compounds is strongly suggestive of the rare earth type.

These properties taken together rather strongly suggest that uranium is partially reverting to an eka-rare-earth cycle, and on this basis it was so arranged.

The present work on elements heavier than uranium, although not yet reported very fully, certainly confirms this arrangement of the elements (2), since plutonium is reported to reach VI state only with definite oxidation, while 95 and 96 become increasingly stable in III state and show chemical properties increasingly similar to those of the more familiar lanthanum family. This gradual change in the actinium family from transition to rare earth types is quite analogous to the effects in the lanthanum family, but being so much more extensive in this arrangement it is indicated by the gradual increase in size of the symbols; this again however is of course not a necessary factor.

In the tabular arrangement neptunium is included as the typical fully developed transition element, since it is reported to give all states from III to VI with fairly uniform ease. Although the chemistry of neptunium is not widely known at present, this will doubtless be corrected.

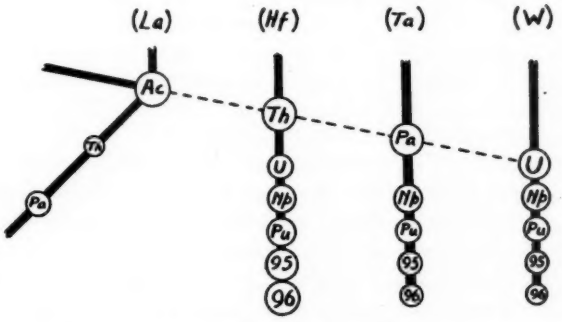

FIG. 4. *The actinium group transition elements.*

In the table, owing to the closeness of elements differing by one unit in atomic number, grouped with thorium in the transition states IV to VI, it is not possible to show all these transitional elements without distortion of the scale. This portion is given fully on the model and is therefore enlarged in Fig. 4.

It might be noted that for convenience in using the model, this extension for the rare earth loops is readily removable, being held in place by two small wooden pins.

General Discussion

It will be seen that all the usual groups of elements are well organized, and, including the transition elements, are clearly separated without overlapping. The usual analytical groups are also closely organized; thus the insoluble chlorides include those of polonium, bismuth, lead, thallium, mercury, copper, and silver. The sulphides insoluble in acids are enclosed roughly in the line through selenium, germanium and cobalt, while sulphides insoluble in ammonia pass still further down the table, and it will be seen that these groupings cross the broad divisions of the table, without suggesting that these divisions are artificial.

Other Transitional Effects

A further feature of this arrangement is that all transitional effects can be clearly indicated and their origin understood. These transitional effects are in reality the basis of the usual tabular classifications in which *A* and *B* columns of elements are placed together, but in the usual columnar table the origin and limits of these effects are not clear.

The transitional effects noted with vanadium have already been discussed in some detail, and the effect shown to exist as far as manganese along the development line. Although transition effects with chromium and manganese are limited to chromates, manganates, and permanganates, within these classes the transition effect is very strong, as similarity to the sulphur and chlorine analogues is very close. This transition however does not extend to the next heavier family, columbium and molybdenum.

The cerium–praseodymium transition has also been discussed and the effects noted in the actinium family. In this latter family the transition region might be considered as greater than any transition shown elsewhere in the table, but it should be noted that the vanadium-manganese transition bridges the range from group IV to group VII elements, or covers the same range as that shown by the actinium family from groups III to VI. This latter group is peculiar in that so many elements show this effect, but when it is noted that this is a rare earth group, where elements are not expected to differ greatly, and also that the increased ionic radii greatly stimulate polyvalence, the effects noted do not appear greater than those that should be expected.

A further type of transition is however noted following nickel, palladium, and platinum. These elements are at the turning point of the loops, and are the end members of an inner electron process. This process reaches its limit at nickel, palladium, and platinum, and these elements show a remarkable inertness (in which property platinum shows the greatest development), differing only in degree from that of the entirely inert zero group. This group therefore functions as another starting point for the additon of peripheral valence electrons in a somewhat similar manner to the development of the active

metals. The chemistry of the elements produced by this process, starting with the copper family, is however greatly different and much more complex than the effects noted in the sodium family with its single valence electron and absolutely inert core.

It will be seen therefore that the development of the 'front' of the table from lithium on the left resembles somewhat the development of the 'back' of the table from copper on the right, and as more valence electrons are added in each case the similarity becomes more marked. Thus when four electrons are added to both series the resulting elements are so similar that they are classed as the main silicon branched families. When still more valence electrons are added, the differences become more marked again but, for the elements grouped round sulphur and those grouped round molybdenum, their acid forming properties in both cases are major features of their chemistry. Thus the 'front' and 'back' of the table develop throughout with much similarity, and it is felt that this arrangement illustrates this effect much more clearly than previous methods.

Transition Effects with Copper, Silver, and Gold

When nickel–palladium–platinum are considered in detail it is clear that the greater stability of the palladium core confers almost definite monovalence on silver, although a few divalent silver compounds are known. With copper and gold however the lesser stability of the nickel and platinum cores still permits the ready removal of electrons from these inner levels, and confers higher valence on copper and gold.

Thus copper II, gold III, and silver II in the few cases known to occur, may properly be considered as transition effects of exactly the same class as that defined earlier, as these polyvalent effects relate solely to the change in development occurring at the nickel family considered as a pseudo-zero group.

Reversed Transition

A still different type of transition is also to be considered. Since Nature can hardly recognize 'up' or 'down', or the development of elements from either light or heavy atoms with any special distinction, transition effects as here defined, if valid, should occur with the same definition, i.e., immediately following changes in the development pattern, but considered as starting from the heaviest atoms.

In starting from the heaviest elements and passing clockwise round the table, the first cycles establish the 'normal' pattern for this direction as passing round both extensions, and the first deviation from this pattern occurs at yttrium. The next element, strontium, therefore must be examined for transition effects. Since strontium however has only two electrons external to its absolutely inert core it cannot remain trivalent and assume transitional properties in a manner analogous to the development of ytterbium from lutecium, since this requires trivalence, a condition absolutely impossible with strontium, as only simple ionic compounds need be considered in this part of the table.

On continuing the development pattern, passing round only the main extension, the next change occurs at silicon, and aluminium must therefore be examined in the same manner. It will be seen on the table that aluminium and magnesium are given places in the gallium and zinc families, respectively, since these two elements do show strong transitional effects referring to these positions. In many ways the properties of aluminium and magnesium strongly resemble those of the gallium and zinc families, and in these properties aluminium and magnesium do not resemble the earth families. Thus the respective portions of the properties of aluminium and magnesium are divided accordingly, in the same manner as is done with those of the other transition elements.

Comparison with Mendelejeff Table

It will be seen that the stronger transitional effects here discussed, i.e., those noted for vanadium, cerium, thorium, aluminium, magnesium, and the branched silicon family are the basis for the usual columnar arrangement of the elements into *A* and *B* groups. Thus the real resemblance between these groups is limited to these transition effects, and when these properties are separated in the manner described, the need to consider the *A* and *B* elements in a forced similarity is no longer required It is therefore felt that the present arrangement gives so much more insight into the orderly development and classification of the elements that its somewhat greater complexity is merely a reflection of the actual complexity of chemistry itself. When these complexities are properly separated and grouped their orderly consideration and study are greatly simplified.

Acknowledgments

Grateful acknowledgment is made of useful discussions regarding this arrangement of the elements with Col. E. A. Flood, Department of National Defence; and also of assistance in drafting and constructing the model by Mr. P. Langevin, Mrs. S. Sterns, and Mr. M. Couture.

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THE EQUILIBRIUM DATA AND CRYSTALLIZATION CHARACTERISTICS OF THE SYSTEM: PICRIC ACID – DINITROPHENOL – PICRAMIDE[1]

By A. N. Campbell,[2] E. J. Pritchard,[3] A. J. R. Campbell,[4] and M. L. Boyd[3]

Abstract

The equilibrium data of the systems: picramide – 2,4-dinitrophenol and picric acid – picramide, have been obtained. The ternary eutectic of the system picric acid – picramide – dinitrophenol has also been obtained. Because of the low crystallization velocity of picramide, it appears that the problem of finding a picric acid mixture of the nature of Shellite, i.e., one containing picric acid and dinitrophenol, which should crystallize only slowly at room temperature, so that the cavity produced by contraction should be accessible to refilling and not cause cavitation, is solved by the use of a Shellite mixture of the following composition: 53.0% picric acid, 41.0% dinitrophenol, 6.0% picramide; this mixture melts at 77° C.

The essence of the problem here investigated has been stated in a previous paper (1), viz., the production of a Shellite that would not crystallize, or only slowly crystallize, at room temperature. The work of the previous paper shows little or no approach to a successful solution. In the present paper, a mixture that crystallizes very slowly is described and to this extent the problem is solved. Even so, however, special precautions would have to be taken to ensure that crystallization proceeded in the desired manner, i.e., from the outside of the shell inwards.

Picramide is known to be a substance of very low crystallization velocity. We therefore added picramide to Shellite with the object of so reducing the crystallization velocity that the Shellite might be induced to become vitreous. Presumably, the explosive power would not be much, if at all, reduced, since picramide is itself an explosive. Too much picramide could not be added, lest the melting point were reduced below the service limit.

The component binary systems of the ternary system: picric acid – dinitrophenol – picramide are picric acid – dinitrophenol, picric acid – picramide and picramide – dinitrophenol. Of these, the two former have already been investigated. The system: picric acid – dinitrophenol is the Shellite system, dealt with in our previous paper (1). According to International Critical Tables, the system picric acid – picramide has a eutectic melting at 113.5° C. and containing 25 mole % picramide: the original reference was not available (2). It remained to investigate the binary system: picramide – dinitrophenol.

[1] *Manuscript received November 5, 1946.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2] *Professor of Chemistry and Head of the Department.*
[3] *Holder of a Bursary under the National Research Council of Canada, 1942-1943.*
[4] *Wife of the senior author.*

Our investigation of the ternary system, however, led us to doubt the accuracy of the data given for the picric acid – picramide system, and we therefore investigated this system ourselves; there is no doubt the published data are incorrect.

Experimental

Equilibrium Data

The picramide was supplied by Dr. G. Wright of Toronto University. It had a melting point of 185.5° to 186.5° C. (value given in the literature = 188° to 190° C. (Beilstein)). The preparation was recrystallized from glacial acetic acid, after which it had a melting point of 185.5° to 186.5° C., i.e., the recrystallization had not affected the purity. This recrystallized product was used in the work described below.

The system: picramide – dinitrophenol was first investigated by thermal analysis, with very indefinite results, owing to the low rate of recrystallization of the melts. The results are given in Table I.

TABLE I

Wt. % picramide	Freezing temperature, ° C.	Eutectic temperature, ° C.
0.0 (100 % dinitrophenol)	110.9	—
10	106	None observed
20	100.8	100.0
30	103.9	100.3
40	128.3	100.4
50	146.8	100.6

The system was then investigated by means of the thaw point – melting point method, with much better results. These results are given in Table II.

TABLE II

Wt. % picramide	Thaw point, ° C.	Melting temperature, ° C.
10	100.5	106.2
20	98	101.5
25	99	104.5
30	100.5	113.3
40	100.0	129.5
50	—	143.0
60	—	153.0
70	—	163.0
80	—	173.0
90	102.0	180.5

When the melting point results are plotted, two curves intersecting at 22.5% picramide and a temperature of 100.2° C. are obtained. The eutectic composition was checked by direct experiment: a mixture containing 22.5% picramide had a thaw point of 99.5° C. and a melting point of 101° C.

Density of Liquid Eutectic Mixture

This was determined at 110° C., as $d_4^{110°} = 1.478$. Taking the densities of solid picramide and solid dinitrophenol as 1.762 and 1.683, respectively, the contraction on filling a shell at 110° C., crystallizing, and cooling to room temperature, is roughly 13% of the total volume; this is higher than the contraction of ordinary Shellite.

Viscosity of Liquid Eutectic

TABLE III

Temperature, ° C.	Viscosity, centipoises	Temperature, ° C.	Viscosity, centipoises
110	5.96	95	8.44
106	6.39	91	11.16
100	7.53		

The Ternary Eutectic: Picric Acid – Picramide – Dinitrophenol

The approximate composition of this eutectic was obtained by joining the compositions of the binary eutectics to the opposite angular points of the triangular diagram. The small triangle formed by the intersection of these three straight lines may give an approximation to the ternary eutectic composition, depending on how straight are the binary eutectic troughs. Mixtures in this neighbourhood were prepared and examined by the thaw point – melting point method. The results are contained in Table IV.

TABLE IV

THE TERNARY EUTECTIC: PICRIC ACID – PICRAMIDE – DINITROPHENOL

Point No.	Composition, %			Thaw point, ° C.	Melting point, ° C.
	Picric acid	Picramide	Dinitrophenol		
1	50.0	11.5	38.5	74.0	86.5
2	47.0	16.0	37.0	74.0	98.0
3	41.0	13.5	45.5	—	90.5
4	53.5	5.0	41.5	74.0	77.5
5	53.0	6.0	41.0	74.0	77.0
6	52.0	8.0	40.0	73.5	78.5
7	52.5	7.0	40.5	73.4	79.0
8	52.0	6.0	42.0	73.5	77.1
9	52.0	5.0	43.0	73.5	78.5
10	54.0	6.0	40.0	—	78.3

Point No. 5 has the lowest melting point and therefore the composition of the ternary eutectic cannot be far from 53.0% picric acid, 41.0% dinitrophenol, 6.0% picramide, melting at 77.0° C. Point No. 8 fulfils the eutectic condition almost equally well.

The System: Picric Acid – Picramide

Since the triangle formed by the intersection of the lines drawn from the pure components to the opposite binary eutectic, on the triangular diagram, was displaced considerably from the ternary eutectic composition given above, it seemed to us that the data of the system picric acid – picramide, as given in the International Tables (2) were incorrect. These data are:— eutectic temperature, 113.5° C.; eutectic composition, 25 mole % picramide = 25% picramide by weight. We therefore repeated this system by the thaw point – melting point method, with the results as given in Table V.

TABLE V

EQUILIBRIUM DATA FOR THE SYSTEM: PICRIC ACID – PICRAMIDE

Weight % picramide	Thaw point, ° C.	Melting point, ° C.
10	—	117.0
14	—	115.0
15	112.5–113	114.0
16	112.5–113	114.5
20	113.0	121.0
25	113.0	124.5
40	—	146.0
70	—	168.5

The above data, when plotted, indicate a eutectic composition of 15.5% picramide, melting about 113° C.

Crystallization Characteristics of the Ternary Eutectic

No quantitative measurements were undertaken, as the exigencies of war work called our attention to other things, but the following qualitative observations were made. A large test-tube was filled with the ternary eutectic. Shrinkage took place on cooling, but the melt did not shrink away from the sides of the tube, but from the centre of the free surface. The hollow thus formed could have been filled with more molten explosive. The density of the liquid ternary eutectic was determined at 78.2° C. as $d_4^{78.2} = 1.56$. From this, the contraction on filling (without refilling) results as 9.76% as compared with 10.78% for the binary mixture 55% picric acid – 45% dinitrophenol, and 10.99% for 60% picric acid – 40% dinitrophenol (ordinary Shellite).

Conclusion

The problem of finding a picric acid mixture of the nature of Shellite, i.e., one containing picric acid and 2,4-dinitrophenol which should crystallize only slowly at room temperature, so that the contraction produced should be

accessible to refilling and not cause cavitation, is solved, in our opinion, by the use of a Shellite mixture of the following composition: 53.0% picric acid, 41.0% 2,4-dinitrophenol, 6.0% picramide: this mixture melts at 77° C.

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A STUDY OF SYSTEMS INVOLVING TRINITROTOLUENE, RDX, NENO, AND DINITROBENZENE, WITH PARTICULAR REFERENCE TO THE COMPOSITION OF THE BINARY EUTECTICS[1]

By A. N. Campbell[2] and H. A. Kushnarov[3]

Abstract

The eutectic temperature and composition were determined by thermal analysis for the systems: TNT–RDX, TNT–NENO, and DNB–NENO. The velocity of crystallization of pure RDX, as well as of the eutectic mixture of TNT–RDX, was studied. Density determinations were made on the pure materials, TNT, RDX, NENO, and DNB, as well as on the eutectic mixtures mentioned above. Where possible, the densities of both molten and solid forms were determined, and the contraction on solidification calculated. An attempt was made to establish the existence of a transition point in the allotropic transformations of NENO. The attempt failed, possibly because the allotropy is monotropic: there seems no reason to doubt the existence of allotropic modifications of NENO.

Introduction

The most satisfactory method of shell filling consists in pouring the molten explosive into the shell and allowing it to solidify slowly. This requires that the material in question should have a melting point that is easily accessible under factory conditions, that is, below the temperature of saturated steam. In this respect trinitrotoluene has proved to be ideal, since its melting point is 80.8° C. When, however, an explosive is mixed with another substance, the melting points of both are lowered, in the absence of solid solution or complete immiscibility in the liquid state. In a simple binary system, the eutectic mixture has the lowest melting point and therefore a knowledge of the eutectic temperature and composition in any binary explosive system is of the highest importance in this connection. Since RDX and NENO are too sensitive to be used unmixed, the eutectic conditions of their admixture with TNT become of interest.

Not only is an upper limit of melting point imposed by factory conditions, but conditions of service impose a lower limit. This lower limit is considered to be about 60° C., since, under tropical or accidental conditions, the temperature of a filled shell might approach this. If incipient, that is, eutectic, melting were to take place below this temperature, the efficiency might be reduced or destroyed, or it might even become a danger to the user. Thus, mixtures used for shell filling should have eutectics lying between 60° and 100° C.

It is well known that most liquids contract on solidification. If a molten explosive cools within a shell, the contraction resulting upon solidification may lead to serious cavitation. If the cavity occurs under the booster, the

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shell may fail to explode, or the shock of the set-back across a cavity in the rear of the charge may cause the shell to explode prematurely. If the contraction occurs at the top of the charge, the cusp formed may be filled up with more liquid explosive, but if cavities occur throughout the body of the cast, this is not possible. The former state of affairs is more likely to be produced if crystallization occurs slowly, and this can be brought about by adding to the melt a substance that reduces velocity of crystallization.

An ideal explosive, from the point of view of cavitation, would be one in which the density of the melt is identical with that of the solid form. Such a substance would show no contraction on solidifying and the problem of cavitation would be almost entirely eliminated. The new explosive NENO appears to approach this requirement, since, it is said, the density of supercooled liquid NENO at 30° C. is 1.63 gm. per cc., while the density of the solid, at the same temperature, is 1.67 gm. per cc., giving a contraction on solidification of only 3.4%. NENO may be cooled to room temperature without crystallization taking place, that is, it enters the vitreous state. Trinitrotoluene, on the other hand, undergoes spontaneous crystallization before it can be cooled to a point where it might be expected to form a glass.

The first aim of the present work was to discover whether mixtures of TNT with RDX and with NENO and of *m*-dinitrobenzene with NENO possessed melting points suitable for shell filling by pouring and to find the eutectic compositions, since a suitable mixture would have, in general, a composition not differing greatly from that of the eutectic. The second aim was to reduce the contraction on solidification of any or all of the above mixtures, by reducing the velocity of crystallization and, if possible, causing them to enter the vitreous state.

Experimental

Materials

Trinitrotoluene.—The TNT used in this work was a commercial explosive, which was not further purified, since our interest lay in the behaviour of the factory produced materials, rather than in pure substances.

RDX.—Pure RDX is said to melt at 202° C., and, on this basis, the material with which we were supplied was markedly impure, since it melted at 195.0° C. After the material had been recrystallized from hot acetone and dried over sulphuric acid, the melting point rose to 198.5° C. Further recrystallizations raised the melting point to 199.5° C., but no higher.

NENO.—The melting point of NENO has been variously stated to lie between 88.5° and 91° C. It appears, however, that earlier preparations were impure and that the true melting point lies between 90° and 91° C. Our material melted at 90.6° C. and therefore was presumably very pure. NENO is reported to be stable up to 105° C. but above that temperature substantial quantities of gas are evolved. Even at 95° C., however, decomposition sets in if the temperature is maintained long enough, say 30 min. NENO is said to exist in two crystalline modifications, an α-form consisting

of needles, and a β-form of twinned rhombs. Since a transition temperature of 38° C. is reported, the dimorphism must be enantiotropic. Such allotropic changes in explosive material may be very undesirable, for example, the 32° C. transition of ammonium nitrate is a well known source of trouble. This effect is due to a difference in density of the two modifications and consequent change in volume, which tends to cause a disruption of the charge. It has been shown, however, that while α-NENO has a density of 1.71 that of β-NENO is 1.69; the change in volume accompanying the allotropic change is therefore slight.

**m-Dinitrobenzene.*—Pure *m*-dinitrobenzene melts at 89.9° C.; our commercial product melted originally at 85° to 87° C., but after two recrystallizations from hot alcohol the melting point rose to 89.6° C.

Apparatus

All thermometers were calibrated against standards. The thaw point – melting point apparatus used in this work has been described elsewhere (2). It is therefore unnecessary to describe it here, but the advantage of the method for at least a preliminary survey of systems of which the components are either rare or explosive may once again be stressed.

The apparatus for determining velocity of crystallization has also been previously described (2).

Thermal analysis was carried out in a small tubular electric furnace, using Plato's method of graduated cooling (5).

A special apparatus was devised to determine the amount of 'sweating' of a given mixture at a given temperature, i.e., the amount of liquid exuding from the cartridge. It consisted of a long glass cylinder, about 2 in. in diameter, placed vertically in a thermostat. A 20 gm. cartridge of the desired composition was then cast in a mould, and, as the liquid was solidifying, the end of a wire was inserted in it. A weighed crucible was placed at the bottom of the cylinder and the cartridge suspended immediately above it so that it hung freely without touching the sides of the cylinder. The open end of the cylinder was corked and a thermometer inserted in the cork so that the bulb was immediately above the suspended cartridge. The crucible was removed and weighed at regular intervals so that the fraction of the cartridge that had melted out could be determined.

Other procedures, such as the use of the dilatometer and of a microscope with heated substage, are too well known to require description.

Results

The equilibrium data, obtained by the thaw point – melting point method, for the system TNT–RDX are contained in Table I (*a*), while the same data for the same system by the method of thermal analysis are contained in Table I (*b*). Table II gives the results of calculating the course of the freezing

**NOTE.—Throughout the paper the abbreviation DNB is used for m-dinitrobenzene.*

curve for the very dilute range, from the van't Hoff formula, $\triangle T = mK_f$. Tables III (*a*) and III (*b*) reproduce the equilibrium data, by the method of thaw point – melting point and by the method of thermal analysis, for the system TNT–NENO. Table IV contains similar data by the thaw point – melting point method only, for the system NENO–DNB. Measurements of velocity of crystallization are given in Tables V (*a*), V (*b*), and V (*c*). The 'sweating' data, i.e., the percentage amounts melted from a cartridge of given composition at a given temperature in a given time, are reproduced in Table VI (*a*), (*b*), (*c*), (*d*) (*e*). Various density determinations are contained in Table

TABLE I (*a*)

THE EQUILIBRIUM DATA OF THE SYSTEM TNT–RDX BY THE THAW POINT – MELTING POINT METHOD

Composition, wt. % of RDX	Thaw point, ° C.	Melting point, ° C.
0	76.5	80.2
2	74.8	79.2
4	74.6	79.0
5	75.0	78.7
6	75.1	92.3
7	74.9	103.5
8	75.3	110.8
9	75.0	114.3
10	74.9	117.0
12	74.7	122.0
14	—	126.2
15	74.9	131.5
18	75.5	135.5
20	75.2	140.0
25	74.9	145.8
30	75.0	155.5
35	75.1	159.5
40	74.9	163.5
50	75.0	172.0
60	75.1	177.5
70	74.8	183.0
80	*	*
90	*	*
100	—	198.5

* *Considerable decomposition made these determinations unreliable.*

TABLE I (*b*)

THE EUTECTIC TEMPERATURE OF THE SYSTEM TNT–RDX BY PLATO'S METHOD OF THERMAL ANALYSIS

Composition, wt. % RDX	Eutectic temp., ° C.	Composition, wt. % RDX	Eutectic temp., ° C.
10	78.4	30	78.0
15	77.9	40	77.8
20	78.1		

TABLE II

MELTING POINTS OF TNT CONTAINING SMALL QUANTITIES OF RDX

K = 111.7° C. per 100 gm. TNT

% RDX	ΔT, calc.	Melting point, ° C. (calc.)	Melting point, ° C. (obs.)	Mol. wt. of RDX
2	1.1	79.1	79.2	228
3	1.7	78.5	—	—
4	2.3	77.9	79.0	389
5	2.9	77.3	78.7	390

TABLE III (*a*)

THE EQUILIBRIUM DATA OF THE SYSTEM TNT–NENO BY THE THAW POINT – MELTING POINT METHOD

Composition		Thaw point, ° C.	Melting point, ° C. (expt.)	Melting point, ° C. (calc.)[1]
Wt. % of NENO	Mol. % of NENO			
0	0	78.7	80.4	—
5	3.2	64.6	78.9	78.8
10	6.6	58.2	77.3	77.0
15	10.1	56.6	75.7	75.3
20	13.7	55.4	74.3	73.4
30	21.4	55.6	70.1	68.9
40	29.7	55.2	66.8	63.9
50	38.9	55.6	62.0	57.8
52	40.9	55.3	60.6	—
54	42.9	55.1	62.1	—
60	48.8	55.1	66.2	65.8
70	59.7	55.5	71.9	72.4
80	71.7	55.2	78.2	78.6
90	85.2	55.8	84.7	84.8
95	92.4	60.2	87.8	87.7
100	100	89.7	90.6	—

[1] *The theoretical values for the melting points of the various mixtures were calculated by means of the Washburn and Read equation (7),*

$$\log_{10} x_a = \frac{-L_a}{2.303R} \cdot (1/T - 1/T_0),$$

where x_a = mole fraction in solution of component crystallizing as solid phase, T_0 = absolute melting point of pure substance, T = equilibrium temperature, R = gas constant, L_a = latent heat of fusion of pure A per mole.

VII. Table VIII records the decrease in density of a sample of NENO kept at 92.6° C. for increasing periods of time. The section concludes with an attempt to find the transition point of NENO dilatometrically (not in table form).

The eutectic temperature according to the thaw point method is approximately 75.0° C., while the melting point curves intersect at 78.5° C. The method of thermal analysis places the eutectic temperature at 78.1° C.

The composition of the eutectic mixture as indicated by the graph of the results is 5% RDX by weight.

The depression of the melting point of TNT, upon the addition of small quantities of RDX, was calculated from the van't Hoff formula $\triangle T = mK_f$ and K_f itself, the molal freezing point constant from the formula $K_f = RT^2/100\,l$ (where l is the latent heat of fusion per gram of TNT = 22.3 cal. per gm. (6)). The figures of Table II were thus obtained.

No high degree of accuracy is claimed for the above results, but it is surprising that for additions of 4 and 5% RDX, the molecular weight approaches twice the formula value (222).

The eutectic temperature lies at 55.3° C. according to the thaw point and at 60.5° C. from the intersection of the melting point curves. In accordance with this, the eutectic contains 52% by weight or 41% molar of NENO.

TABLE III (*b*)

THE SYSTEM TNT–NENO BY THE METHOD OF THERMAL ANALYSIS

Composition, wt. % NENO	Freezing point, ° C.	Eutectic temperature, ° C. (temp. of complete crystallization)
5	78.5	73.2
10	76.8	68.2
15	75.0	64.6
20	73.0	62.3
25	71.1	60.5
52	59.9	Eutectic mixture

TABLE IV

EQUILIBRIUM DATA OF THE SYSTEM NENO – DNB BY THE THAW POINT – MELTING POINT METHOD

Composition		Thaw point, ° C.	Melting point, ° C. (expt.)	Melting point, ° C.[1] (calc.)
Wt. % NENO	Mole % NENO			
0	0	88.4	89.6	—
10	5.0	57.4	86.8	86.4
20	10.6	57.2	83.2	82.6
30	16.7	56.8	77.6	78.5
40	23.8	56.5	72.8	73.2
50	32.0	56.8	67.7	66.9
60	41.4	56.8	62.6	59.7
61	42.4	56.8	62.3	—
62	43.5	56.9	61.8	—
63	44.6	56.8	63.0	—
70	52.5	57.1	68.2	68.2
80	65.4	57.2	75.6	75.6
90	81.0	57.5	82.8	82.9
100	100	89.7	90.6	—

[1] *The calculated values for the melting points were obtained by means of the Washburn and Read equation (7); the latent heat of fusion of DNB per gram = 25.4 cal. (1).*

The thaw point method and the method of thermal analysis agree fairly well in regard to the melting point, but there is great discrepancy between the two in regard to the thaw point, or temperature of eutectic melting. The solidus line as determined by Plato's method drops so gradually on the TNT side of the diagram that it does not reach the eutectic horizontal until a content of 28% NENO by weight has been attained. Such behaviour is suggestive of solid solution, implying that TNT can dissolve 28% NENO in the solid state.

TABLE V (*a*)

VELOCITY OF CRYSTALLIZATION OF TNT[1]

Temperature, °C.	Degree of supercooling, °C.	C.V.[2], mm. per min.
70.0	10.1	35
60.0	20.1	94
50.0	30.1	126
40.0	40.1	158
30.0	50.1	171
22.0	58.1	127

[1] *These values have been determined by others (2) but are reproduced here in order that they may be compared with the values for the eutectic mixture.*

[2] *The abbreviation C.V. is used throughout the tables to indicate 'crystallization velocity'.*

TABLE V (*b*)

VELOCITY OF CRYSTALLIZATION OF THE TNT – RDX EUTECTIC MIXTURE[1]

Temperature, °C.	Degree of supercooling, °C.	C.V., mm. per min.
71.2	7.3	10.7
68.7	9.8	19.1
63.0	15.5	32.4
58.0	20.5	38.7
48.0	30.5	48.6
38.0	40.5	51.2
28.0	50.5	38.2

[1] *The RDX in this mixture was previously recrystallized from acetone.*

TABLE V (*c*)

VELOCITY OF CRYSTALLIZATION OF THE TNT–RDX EUTECTIC MIXTURE IN WHICH THE RDX WAS PREVIOUSLY SIMMERED WITH WATER

Temperature, °C.	Degree of supercooling, °C.	C.V., mm. per min.
71.2	7.3	7.8
68.5	10.0	14.3
59.1	19.4	28.6
47.5	31.5	35.5
37.5	41.5	35.4
27.8	50.7	32.7

The eutectic temperature, by the thaw point method, lies at 56.9° C., while the melting point curves intersect at 61.7° C. The eutectic composition lies at 62% by weight and 44 mole % of NENO. The eutectic mixture was subjected to thermal analysis and gave a eutectic temperature of 61.2° C. The absence of any discontinuity on the cooling curve prior to the eutectic temperature confirmed the eutectic composition as 62% NENO.

TABLE VI (*a*), (*b*), (*c*), (*d*), (*e*)

SWEATING DATA FOR VARIOUS MIXTURES OF TNT–NENO

Time interval, hr.	% Sweated out	Time interval, hr.	% Sweated out	Time interval, hr.	% Sweated out
VI (*a*). Composition of cartridge: 10% NENO – 90% TNT (by weight). Temperature of thermostat = 63.4° C.					
0	0	146	2.78	357	3.70
24	1.85	167	2.81	406	3.70
69	2.12	238	3.34	430	3.70
94	2.41	294	3.61	—	—
118	2.68	342	3.68	—	—
VI. (*b*). Composition of cartridge: 7% NENO – 93% TNT (by weight). Temperature of thermostat = 63.6° C.					
0	0	116	2.25	285	3.22
44	1.71	164	2.78	—	—
68	1.97	237	2.98	—	—
VI (*c*). Composition of cartridge: 5% NENO – 95% TNT (by weight). Temperature of thermostat = 63.6° C.					
0	0	97	1.32	261	1.83
44	1.06	164	1.62	285	1.83
68	1.17	237	1.83	—	—
VI (*d*). Composition of cartridge: 5% NENO – 95% TNT (by weight). Temperature of thermostat = 61.3° C.					
0	0	48	0.48	168	0.48
24	0.48	96	0.48	—	—

VI (*e*). Thaw points and melting points of sweated extract from Tests (*a*), (*b*), (*c*), and (*d*)

Sweated material from	Thaw point, ° C.	Melting point, ° C.
(*a*)	53.8	59.2
(*b*)	55.1	59.7
(*c*)	54.8	58.8
(*d*)	55.3	59.4

TABLE VII

DENSITY DETERMINATIONS

Substance	Density of liquid gm./cc.	Density of solid gm./cc.	Contraction on cooling to 22° C., %
TNT	d_4^{85} 1.462	d_4^{22} 1.648	11.51
RDX–TNT eutectic	d_4^{85} 1.491	d_4^{22} 1.650	9.80
RDX	*	d_4^{22} 1.761	—
NENO	$d_4^{92.6}$ 1.562	d_4^{22} 1.686	7.80
NENO–TNT eutectic	d_4^{91} 1.545	d_4^{22} 1.678	7.75
m-Dinitrobenzene	d_4^{90} 1.364	d_4^{22} 1.567	12.96

* *It was not possible to determine the density of liquid RDX, because of decomposition just above the melting point.*

TABLE VIII

DECREASE IN DENSITY OF MOLTEN NENO WITH TIME.
TEMPERATURE OF THERMOSTAT = 92.6° C.

Time, hr.	0	1½	2½
Density, gm./cc.	1.562	1.561	1.559

The Transition Point of NENO

No transition point could be detected either dilatometrically or by means of the polarizing microscope. For example, a sample in a dilatometer was slowly heated to 65° C. and kept there for three days. Then it was cooled to −12° C., at which temperature it was again kept for three days. At no time was there any discontinuous movement of the xylene index.

The density determinations on the original material indicated that if two forms exist, the original material was the β-form. This was caused to transform to the α-form by stirring a suspension in chloroform. The densities of the untreated and treated material were as follows:

(*a*) Untreated NENO; $d_4^{22} = 1.686$ gm./cc.

(*b*) NENO stirred in chloroform for fifteen hours: $d_4^{22} = 1.706$ gm./cc.

Discussion of Results

(*a*) *The System: TNT–RDX*

The equilibrium data for this system give rise to two smooth curves intersecting at the eutectic: there is no indication of compound formation. It is surprising, however, that the addition of 5% RDX depresses the freezing point of TNT by only 1.5° C. This could be explained as due to the formation of solid solutions of RDX in TNT, but this is doubtful in view of the constancy of the thaw point for mixtures containing as little as 2% RDX. On the other hand, it is quite possible that the solute RDX is associated in solution in liquid TNT. The apparently high molecular weight of RDX as

calculated from the freezing point depression in Table II tends to support this, but no high degree of accuracy is claimed for these results.

The eutectic temperature as determined by the intersection of the melting point curves (78.5° C.) is in good agreement with direct determination of the eutectic temperature from the cooling curves, viz., 78.1° C., but both these values are about three degrees higher than the thawing temperature. The discrepancy is due to the presence of impurities.

The velocity of crystallization of the TNT–RDX eutectic mixture was determined on two different preparations, using RDX that had been treated differently in the two cases. Table V shows that there is a marked difference in crystallization velocity depending on whether the RDX has been recrystallized from acetone or simmered with distilled water. The crystallization velocity of the former sample was considerably greater, indicating that RDX that has been merely simmered with water contains impurities that are removed by recrystallization from acetone. The presence of 5% RDX reduces the crystallization velocity of TNT to about one-third. Although the magnitude of the reduction is considerable for so small an addition of the second substance, the general behaviour confirms the observation of Moore (4) that the addition of a second component tends to reduce the crystallization velocity of the original material. Finally, both eutectic mixtures exhibit a maximum crystallization velocity, at about 35° to 40° C. of supercooling, in accordance with Tammann's finding (3), but there is no evidence of a region of constant crystallization velocity; the curve rises to a maximum and then falls immediately.

(*b*) *The System TNT–NENO*

The equilibrium diagram for this system also shows no evidence of compound formation. Again the melting point curves are both smooth and they intersect at a temperature of 60.5° C. and at a composition of 52% by weight or 41% molar of NENO. The eutectic temperature by thermal analysis is 59.9° C. The thaw point line again falls below the above values: it lies at 55.3° C. The cause of the discrepancy is the same as in the system TNT–RDX, viz., impure materials.

When the results of both thermal analysis and thaw point method are plotted, it is at once apparent that the eutectic temperature is not reached by any mixture until a content of 20 to 30% NENO is reached. This suggests the possibility of solid solutions. To test this hypothesis, 'sweating' experiments were conducted as described under "Apparatus". Contrary to expectations, a 5% NENO, 95% TNT cartridge lost liquid matter even at 61.3° C., at a temperature 2.7° C. below the supposed solidus line, where no sweating was expected. Moreover, the amount of material exuded decreased as the eutectic temperature of 60.5° C. was approached. This eliminates the possibility of the formation of solid solution.

Examination of the sweating data of Table VI (*a*), (*b*), (*c*), (*d*), (*e*), shows that the amount of liquid exuded is far less than that calculated from the eutectic composition. The reason probably is that a great deal of the melting eutectic is retained within the cavities of the cartridge and only a small portion actually drops away. The thermal analyses in Table VI (*e*) corroborate the eutectic composition of the various sweated extracts.

The theoretical melting points calculated by the equation of Washburn and Read (7) are in fair agreement with the experimentally determined melting points.

(*c*) *The System: TNT–Dinitrobenzene*

In this system the same discrepancy, as before, was encountered in the determination of the eutectic temperature. The melting point curves intersect at 61.7° C., while the eutectic halt lies at 61.2° C. The thaw point horizontal again lies below these two values at 56.9° C. The theoretical values of the melting point as determined from the equation of Washburn and Read agree fairly well with the experimental values.

(*d*) *The Stability of NENO*

The tendency of molten NENO to decompose was confirmed both visually and quantitatively. Table VIII shows that at only 2.0° C. above its melting point there was a decrease in density of 0.001 gm. per cc. at the end of one and one-half hours. After two and one-half hours the decomposition became more pronounced. Qualitatively, bubbles of gas could be observed in the melt at the end of one hour.

(*e*) *Transition Point of NENO*

The transition point of NENO could not be established dilatometrically, although the densities of the samples of NENO before and after treatment with chloroform indicate that an α- and a β-form do exist. It required, however, 15 hr. stirring in chloroform to convert the β-form to the α-form: five hours' stirring had little or no effect. The α-form had a density of 1.706 gm. per cc.

(*f*) *Densities*

The density determinations (Table VII) show that the contractions of the eutectic mixtures on solidifying are in all cases less than those of the pure components. It has already been pointed out that a diminished contraction is a desirable characteristic from the point of view of shell filling.

Conclusion

As this work was dicatated by war exigencies, it cannot be claimed that any systematic scheme has been pursued or definite conclusion arrived at. We feel, however, that these extensive data, disconnected as they are, cannot be without interest to future workers with the new explosives RDX and NENO.

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A METHOD OF ANALYSIS FOR THE SYSTEM: BENZENE – ETHYL ALCOHOL – CARBON TETRACHLORIDE[1]

By A. N. Campbell[2] and S. I. Miller[3]

Abstract

The densities and refractive indices (N_c) of binary and ternary mixtures of benzene, ethyl alcohol, and carbon tetrachloride have been determined at 25° C. From these data, a method for the analysis of ternary liquid mixtures of these components has been developed. The limit of accuracy in the analysis of ternary mixtures of the pure components is 0.3%. The method can be applied to the analysis of commercial materials with an accuracy of 2.0%.

Introduction

The subject matter of this paper represents a preliminary step in the study of the isobaric distillation of the ternary mixture named in the title. In order to determine the compositions of equilibrium liquid and vapour phases a rapid and accurate method of analysis was required. Any chemical analysis would have been protracted and inaccurate, even if it were possible. We were therefore obliged to use purely physical methods.

Benzene, ethyl alcohol, and carbon tetrachloride are miscible in all proportions, and, just as one physical property is sufficient to fix the composition of a binary mixture, two will determine the composition of a ternary. We chose refractive index and density as suitable properties, since they can be determined readily and accurately on relatively small quantities of liquid (10 cc.): this was a necessary condition for our work since the quantity of condensed vapour was necessarily small. The method is not new: Barbaudy (1) analysed in this manner ternary mixtures of benzene, alcohol, and water, with an accuracy of 0.25%. We claim an accuracy of 0.2%, a high degree of accuracy for the analysis of an organic system.

Obviously, prior to the analysis of any particular system, a complete calibration must be carried out, i.e., the densities and refractive indices must be determined over the complete range of mixtures, the composition being known.

Previous Investigations

(*a*) *Benzene–Alcohol*

Barbaudy (1), studying the ternary system benzene – alcohol – water, determined the densities and refractive indices (N_D) at 25° C. Other workers (11, 16), whose results were not available, have supplied similar data at other temperatures.

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The majority of Barbaudy's density values coincide with our experimental curve given in Fig. 1. His figures for refractive index (N_D) generally parallel those for N_c obtained by us (Fig. 2).

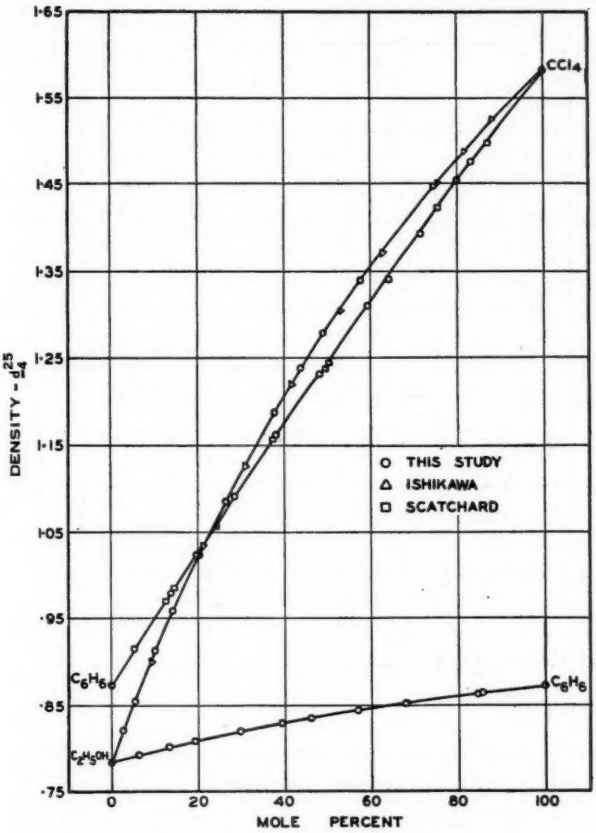

FIG. 1. *The binary systems—previous investigations—*d_4^{25}.

(*b*) *Carbon Tetrachloride–Alcohol*

King and Smedley (10) determined densities for this binary very crudely. Ishikawa and Yamaguchi (9) determined the densities and used them for purposes of analysis. The density of their alcohol indicates a small water content of 0.3%, while their carbon tetrachloride also differs slightly from the material used in this study. Nevertheless, Fig. 1 shows that these small deviations affect but little the comparison between their work and ours.

Curtis and Titus (5) determined densities and refractive indices (N_D) at 19.4° C., as a part of their study of the ternary system carbon tetrachloride – alcohol – water. Their refractive index curve runs parallel to ours for N_c.

(c) Benzene – Carbon Tetrachloride

Brown (3, 4) found densities for this binary mixture at 20° C. In a similar study, Wood and Brusie (22) evaluated thermodynamic functions from density–composition results at 30° C.

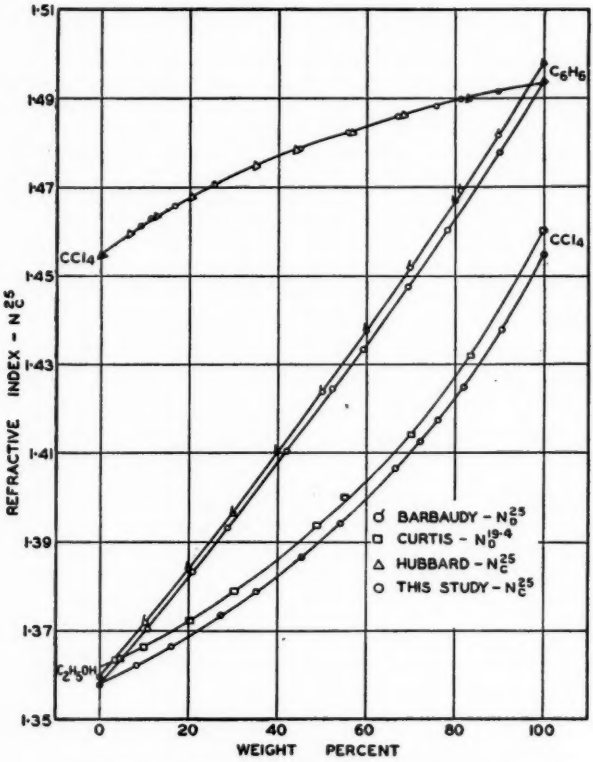

FIG. 2. *The binary systems—previous investigations—N_c^{25}.*

Rosanoff (17) and Zawidzki (23) determined the refractive indices at 25.2° C., for purposes of analysis.

McMillan and McDonald (13) found densities at 27° C. and refractive indices (N_D) at 25° C. They do not claim more than 1.0% precision: moreover the properties of their materials indicate substantial amounts of impurity.

Scatchard, Wood, and Mochel (18) determined densities at 25° C. Their values are compared with ours in Fig. 1.

Hubbard's results (7, 8) for densities and refractive indices (N_D, N_c, etc.) of various binary systems, including benzene – carbon tetrachloride, are quoted in International Critical Tables. His N_c data are compared with ours in Fig. 2.

Experimental

Purification of Materials

Benzene

B.D.H. 'Analar' benzene was used, without further purification. This material is so good, as revealed by its density and refractive index, that attempted purification could not have improved it.

Carbon Tetrachloride

'Analar' carbon tetrachloride was fractionally distilled over phosphorus pentoxide, and the fraction distilling within a 0.2° C. range used.

Ethyl Alcohol

The ordinary concentrated alcohol of commerce (6% water) was refluxed with 12 *N* sulphuric acid and distilled. The middle distillate was treated with sodium hydroxide and silver nitrate, refluxed, and distilled, the middle distillate only being collected. This distillate was then treated with several successive portions of lime, which had been calcined at 1000° C. After standing for several days over lime, this alcohol was decanted, refluxed with fresh lime, and fractionated.

The first and last fractions were rejected and the alcohol collected over a 0.2° C. range. This alcohol had a water content of less than 0.07%, judging from its density.

Published properties of 'pure' materials differ, indicating frequently that the materials used were not really pure. The best figure for the density of alcohol is that determined at the Bureau of Standards by Osborne, McKelvey and Bearce (15). Table I reveals the differences in the properties of materials used by various workers.

TABLE I

Purity of materials

Source	Benzene			Ethyl alcohol			Carbon tetrachloride		
	d_4^{25}	N_c^{25}	N_D^{25}	d_4^{25}	N_c^{25}	N_D^{25}	d_4^{25}	N_c^{25}	N_D^{25}
This study	0.87376	1.49331	1.49797	0.78524	1.35767		1.58455	1.45478	
Ishikawa (9)				0.7860			1.5842		
Barbaudy (1)	0.87363		1.49795	0.78506		1.3592			
Scatchard (18)	0.87370						1.58426		
McMillan (13)	$0.8734^{27°}$		1.4985				$1.5866^{27°}$		1.4549
Osborne (15)				0.78506					
Martin (14)	0.87288	1.49312							
Hubbard (7, 8)	0.87372	1.49330	1.49794				1.58456	1.45464	1.45732
Varteressian (21)	0.8727		1.4976	0.7852		1.3598			

Procedure

Temperature Control

The temperature of the thermostat was 25.0° ± 0.03° C. Thermostat water circulated around the refractometer gave a temperature of 25.0° ± 0.05° C.

Preparation of Mixtures

When the components are volatile, it is not so easy to prepare a mixture of accurately known composition. We prepared our mixture by weighing in 100 cc. long-necked, glass stoppered flasks. Such weights of components were chosen that the flask was always filled into the narrow neck, in order to reduce change of composition by volatilization. Weighings to six, sometimes five, significant figures were usual. Percentage compositions are listed to four figures, although three figures are sufficient for the attainable accuracy of analysis. The following factors lead to uncertainty in the fourth figure: (i) omission of buoyancy correction; (ii) leakage at ground glass stoppers; (iii) evaporation on opening flasks or transferring liquids. These errors are to some extent compensatory, and the composition figures are accurate to better than 0.1%.

Refractive Index Measurements

A Pulfrich refractometer was used, with water circulation at 25° C. The H_ϵ line of the hydrogen discharge tube was used for the measurements.

Prolonged observations gave drifting readings, because of a slow fractional distillation from the liquid in the cell. Therefore the cell and the liquid mixture, in a separate stoppered container, were both brought to 25° C. before filling the cell of the refractometer.

Density Determinations

For such volatile mixtures as these, we found the Weld specific gravity bottle best. This pycnometer has a ground glass cap that reduces evaporation to a minimum. As with the determinations of refractive index, the mixture was first brought to 25° C. in stoppered containers in the thermostat before filling the pycnometer.

Since our results were to be used directly in analysis, the weights of liquid and of calibrating water held by the pycnometer were not corrected for buoyancy. Since the bottles were counterpoised, variation in buoyancy did not affect the results. Nevertheless, it should be noted that not all the densities of this paper are corrected to vacuum. Wherever a comparison between our results and those of other workers is made, this correction has been introduced, e.g., in Fig. 1. The symbol $\underline{d}_4^t$ is used for corrected density, and d_4^t for uncorrected. To convert the densities given in this paper to vacuum or absolute densities, a table (Table II) of correction factors is supplied.

Experimental Results

The experimental results follow in tables. Since the direct determinations of density and refractive index were exceedingly numerous (there were about 250 such), they are not given in this paper. Instead of this, Tables III and IV give the isodensity and isofract data. These were obtained by plotting the experimental data for each pseudobinary system as a family of curves and drawing lines of equal density and equal refractive index through them.

At the top of each column in Tables III and IV are given the fixed ratios of the pseudobinaries. From these data the triangular diagram of Fig. 7 was obtained. The other tables are explained under Discussion.

TABLE II

CORRECTIONS FOR ANALYTIC DENSITIES, d_4^{25}, TO VACUUM d_4^{25}

Over 1.55	−0.0007	1.12 −1.25	−0.0002
1.45–1.55	−0.0006	1.04 −1.12	−0.0001
1.36–1.45	−0.0005	0.955–1.04	0.0000
1.29–1.36	−0.0004	0.870–0.955	+0.0001
1.25–1.29	−0.0003	0.785–0.870	+0.0002

Discussion of Results

(*a*) *Experimental Curves*

An orderly method of obtaining and assembling data in ternary systems is afforded by the use of pseudobinary curves. Schreinemakers (19, 20), for example, used this method of tabulating his vapour pressure data. It consists simply in adding to a fixed binary mixture varying amounts of the third component. If the binary mixture is treated as one component, it is possible to plot any property against composition on a rectilinear diagram. Figs. 3 to 6 express the experimental results, as determined directly.

Ternary mixtures were made up of binary mixtures of benzene–alcohol or carbon tetrachloride–alcohol to which carbon tetrachloride or benzene, respectively were added. In Fig. 3, for example, the figures on the left represent the percentage of benzene in the binary, benzene–alcohol. To each of these, carbon tetrachloride was added, giving rise to isothermal density–composition curves, all of which end at the density of pure carbon tetrachloride. Fig. 4 gives curves of refractive index for the same mixtures. Figs. 5 and 6 are analogous, the initial binary being carbon tetrachloride–alcohol. (In Fig. 5, in order to separate the curves, each curve has the indicated scale moved vertically by a multiple of 0.0100 density units: all curves should coincide at the density of pure carbon tetrachloride, for 100% carbon tetrachloride.)

Theoretically, one binary mixture, e.g., alcohol–benzene, should be sufficient to give all the required data, but one binary set supplements the other in regions where data are scanty, although considerable overlapping does occur in the central portions of Figs. 4 and 6. This will be more obvious when Fig. 7 is discussed.

(*b*) *Calibration Diagram*

Fig. 7 scaled down from the actual calibration diagram is based on points taken from the experimental curves. Lines running from the base upwards are lines of constant density, isodensity lines: lines sloping generally from the left side to the base are lines of constant refractive index, isofracts (Bowen (2)). The triangular diagram was constructed as follows. Horizontals, cutting the

rectangular experimental curves in Figs. 3 to 6 gave sets of composition data corresponding to constant densities (Table III) and constant refractive indices (Table IV). Every sequence obtained for a constant density from Figs. 3 and 5 gave an isodensity line in Fig. 7; every sequence obtained from Figs. 4 and 6 for a constant refractive index gave an isofract in Fig. 7.

TABLE III (*a*)

DERIVED ISODENSITY DATA

CCl_4 / C_2H_5OH	0 / 100	8.76 / 91.24	16.45 / 83.55	27.32 / 72.68	35.57 / 64.43	45.81 / 54.19	54.44 / 45.56	66.9 / 33.1	72.36 / 27.64	82.09 / 17.91	90.73 / 9.27	100 / 0
d_4^{25}	Per cent C_6H_6 in ternary											
0.800	18.00	—	—	—	—	—	—	—	—	—	—	—
0.820	41.72	—	—	—	—	—	—	—	—	—	—	—
0.840	64.70	36.80	—	—	—	—	—	—	—	—	—	—
0.860	87.04	76.90	24.10	—	—	—	—	—	—	—	—	—
0.880	—	—	—	80.30	90.90	94.36	95.78	97.12	97.50	97.98	98.04	98.38
0.900	—	—	—	27.40	64.16	78.87	84.22	88.48	89.77	91.44	92.46	93.37
0.920	—	—	—	—	40.90	64.18	73.17	80.34	82.42	85.30	87.12	88.73
0.940	—	—	—	—	19.00	50.22	62.92	72.53	75.46	79.42	82.00	84.17
0.960	—	—	—	—	—	36.98	52.98	65.08	68.83	73.81	77.08	79.77
0.980	—	—	—	—	—	24.33	43.20	58.00	62.46	68.44	72.40	75.62
1.000	—	—	—	—	—	12.20	33.68	51.23	56.48	63.36	67.86	71.68
1.020	—	—	—	—	—	1.16	24.62	44.80	50.70	58.42	63.52	67.93
1.040	—	—	—	—	—	—	16.23	38.68	45.13	53.67	59.37	64.36
1.060	—	—	—	—	—	—	8.23	32.78	39.74	49.14	55.37	60.98
1.080	—	—	—	—	—	—	1.28	27.00	34.58	44.78	51.53	57.68
1.100	—	—	—	—	—	—	—	21.44	29.60	40.57	47.82	54.53
1.120	—	—	—	—	—	—	—	16.10	24.80	36.56	44.27	51.42
1.140	—	—	—	—	—	—	—	11.02	20.19	32.63	40.90	48.38
1.160	—	—	—	—	—	—	—	6.23	15.78	28.79	37.61	45.46
1.180	—	—	—	—	—	—	—	1.47	11.46	25.13	34.43	42.42
1.200	—	—	—	—	—	—	—	—	7.40	21.60	31.37	39.56
1.220	—	—	—	—	—	—	—	—	3.37	18.23	28.30	36.77
1.240	—	—	—	—	—	—	—	—	—	14.98	25.32	34.12
1.260	—	—	—	—	—	—	—	—	—	11.74	22.44	31.60
1.280	—	—	—	—	—	—	—	—	—	8.62	19.94	29.21
1.300	—	—	—	—	—	—	—	—	—	5.73	17.66	26.87
1.320	—	—	—	—	—	—	—	—	—	2.86	14.47	24.62
1.340	—	—	—	—	—	—	—	—	—	0.03	12.03	22.42
1.360	—	—	—	—	—	—	—	—	—	—	9.63	20.33
1.380	—	—	—	—	—	—	—	—	—	—	7.36	18.22
1.400	—	—	—	—	—	—	—	—	—	—	5.12	16.22
1.420	—	—	—	—	—	—	—	—	—	—	2.93	14.30
1.440	—	—	—	—	—	—	—	—	—	—	0.76	12.42
1.460	—	—	—	—	—	—	—	—	—	—	—	10.52
1.480	—	—	—	—	—	—	—	—	—	—	—	8.73
1.500	—	—	—	—	—	—	—	—	—	—	—	6.98
1.520	—	—	—	—	—	—	—	—	—	—	—	5.29
1.540	—	—	—	—	—	—	—	—	—	—	—	3.63
1.560	—	—	—	—	—	—	—	—	—	—	—	2.04
1.580	—	—	—	—	—	—	—	—	—	—	—	0.42

Each of the experimental curves in Figs. 3 to 6 had two components in a fixed weight ratio. These fixed ratios of composition are represented by the fainter lines originating from the benzene and carbon tetrachloride corners in Fig. 7. All derived data fall on these lines, and indeed, the drawing up of the triangular analysis diagram is greatly simplified if these lines are drawn in first.

TABLE III (*b*)

DERIVED ISODENSITY DATA

$\frac{C_6H_6}{C_2H_5OH}$	$\frac{0}{100}$	$\frac{10.69}{89.31}$	$\frac{21.01}{78.99}$	$\frac{28.94}{71.06}$	$\frac{42.05}{57.95}$	$\frac{52.55}{47.45}$	$\frac{59.26}{40.74}$	$\frac{69.30}{30.70}$	$\frac{78.38}{21.62}$	$\frac{90.28}{9.72}$
d_4^{25}	Per cent CCl_4 in ternary									
0.800	3.54	1.47	—	—	—	—	—	—	—	—
0.820	8.24	6.23	4.16	2.53	—	—	—	—	—	—
0.840	12.79	10.88	8.92	7.32	4.66	2.53	1.13	—	—	—
0.860	17.14	15.40	13.53	12.00	9.40	7.24	5.92	3.99	1.97	—
0.880	21.21	19.63	17.93	16.45	14.00	11.93	10.60	8.78	6.77	4.07
0.900	25.12	23.42	22.01	20.58	18.38	16.44	15.22	13.40	11.57	8.93
0.920	28.94	27.18	25.97	24.46	22.57	20.79	19.53	17.78	16.06	13.60
0.940	32.53	30.79	29.73	28.28	26.50	24.58	23.66	21.90	20.30	18.03
0.960	35.96	34.33	33.33	32.00	30.27	28.30	27.56	25.87	24.38	22.24
0.980	39.27	37.66	36.77	35.62	33.87	31.99	31.30	29.64	28.33	26.14
1.000	42.42	40.69	40.02	39.03	37.34	35.52	34.96	33.37	32.06	30.00
1.020	45.42	43.70	43.12	42.30	40.63	38.98	38.37	36.98	35.67	33.70
1.040	48.27	46.66	46.20	45.46	43.82	42.25	41.66	40.46	39.11	37.34
1.060	51.10	49.57	49.21	48.48	46.88	45.46	44.86	43.78	42.38	40.74
1.080	53.86	52.41	51.97	51.37	49.93	48.56	47.97	46.87	45.62	44.06
1.100	56.54	55.18	54.66	54.13	52.75	51.47	50.96	49.90	48.75	47.24
1.120	59.13	57.80	57.26	56.61	55.54	54.38	53.78	52.80	51.76	50.36
1.140	61.56	60.32	59.81	59.17	58.21	57.12	56.38	55.64	54.67	53.37
1.160	63.94	62.68	62.24	61.64	60.80	59.80	59.30	58.42	57.53	56.23
1.180	66.23	65.03	64.64	64.12	63.24	62.40	61.76	61.03	60.20	58.47
1.200	68.43	67.33	66.98	66.55	65.67	64.82	64.23	63.56	62.60	61.68
1.220	70.58	69.58	69.24	68.82	68.00	67.19	66.68	66.06	65.82	64.24
1.240	72.63	71.70	71.44	71.03	70.23	69.52	69.08	68.43	67.43	66.78
1.260	74.64	73.74	73.53	73.20	72.42	71.78	71.38	70.71	69.74	69.21
1.280	76.59	75.75	75.54	75.27	74.58	73.99	73.57	72.98	72.06	71.54
1.300	78.46	77.68	77.56	77.27	76.62	76.08	75.67	75.06	74.36	73.78
1.320	80.36	79.59	79.43	79.18	78.66	78.17	77.78	77.13	76.54	75.99
1.340	82.10	81.40	81.32	81.07	80.63	80.17	79.77	79.17	78.64	78.17
1.360	83.83	83.20	83.15	82.90	82.51	82.12	81.67	81.18	80.73	80.22
1.380	85.53	84.95	84.91	84.67	84.33	84.00	83.58	83.09	82.73	82.25
1.400	87.16	86.67	86.58	86.42	86.06	85.79	85.46	85.00	84.63	84.21
1.420	88.72	88.37	88.24	88.03	87.80	87.50	87.23	86.80	86.54	86.13
1.440	90.22	89.99	89.83	89.70	89.52	89.21	88.98	88.62	88.31	87.99
1.460	91.70	91.57	91.37	91.26	91.20	90.86	90.63	90.36	90.20	89.78
1.480	93.15	93.01	92.87	92.77	92.71	92.46	92.26	92.00	91.89	91.54
1.500	94.54	94.44	94.34	94.23	94.19	94.02	93.83	93.61	93.56	93.25
1.520	95.86	95.83	95.73	95.66	95.64	95.55	95.35	95.20	95.14	94.88
1.540	97.18	97.17	97.07	97.04	97.02	96.97	96.81	96.73	96.66	96.47
1.560	98.42	98.43	98.37	98.37	98.37	98.36	98.29	98.20	98.15	98.04
1.580	99.62	—	—	—	—	—	—	—	—	99.54

TABLE IV (*a*)

DERIVED ISOFRACT DATA

CCl_4 / C_2H_5OH	0 / 100	8.76 / 91.24	16.45 / 83.55	27.32 / 72.68	35.57 / 64.43	45.81 / 54.19	54.44 / 45.56	66.9 / 33.1	72.36 / 27.64	82.09 / 17.91	90.73 / 9.27	100 / 0
N_c^{25}	Per cent C_6H_6 in ternary											
1.360	1.93	—	—	—	—	—	—	—	—	—	—	—
1.365	6.17	2.54	—	—	—	—	—	—	—	—	—	—
1.370	10.34	6.66	3.06	—	—	—	—	—	—	—	—	—
1.375	14.38	10.73	7.14	1.49	—	—	—	—	—	—	—	—
1.380	18.42	14.83	11.22	5.66	0.94	—	—	—	—	—	—	—
1.385	22.43	18.83	15.26	9.82	5.03	—	—	—	—	—	—	—
1.390	26.38	22.82	19.39	13.99	9.22	2.84	—	—	—	—	—	—
1.395	30.25	26.77	23.57	18.16	13.51	7.01	0.65	—	—	—	—	—
1.400	34.18	30.62	27.70	22.21	17.66	11.30	4.67	—	—	—	—	—
1.405	38.07	34.64	31.76	26.35	21.94	15.60	8.66	—	—	—	—	—
1.410	41.90	38.57	35.78	30.56	26.14	19.92	13.16	3.32	—	—	—	—
1.415	45.67	42.52	39.73	34.76	30.40	24.22	17.68	7.80	2.23	—	—	—
1.420	49.42	46.42	43.76	38.94	34.73	28.60	22.24	12.40	6.88	—	—	—
1.425	53.14	50.26	47.78	43.15	39.08	33.13	26.82	17.16	11.63	0.23	—	—
1.430	56.83	54.05	51.78	47.32	43.48	37.70	31.66	22.02	16.68	5.03	—	—
1.435	60.48	57.83	55.72	51.42	47.80	42.41	37.74	27.08	21.88	10.16	—	—
1.440	64.10	61.70	59.62	55.53	52.17	47.07	41.81	32.46	27.26	15.62	2.52	—
1.445	67.63	65.47	63.48	59.66	56.53	51.82	46.90	37.95	32.83	21.40	8.06	—
1.450	71.17	69.24	67.23	63.82	60.90	56.62	52.08	43.50	38.62	27.60	14.16	—
1.455	74.67	72.96	71.18	67.98	65.33	61.50	57.28	49.37	44.63	34.02	20.98	0.28
1.460	78.16	76.60	75.07	72.18	69.88	66.33	62.47	55.24	51.00	40.79	28.48	7.18
1.465	81.56	80.26	78.97	76.55	74.37	71.21	67.73	61.40	57.48	48.00	36.30	15.13
1.470	84.96	83.80	82.77	80.83	78.93	76.13	73.20	67.63	64.24	55.67	44.84	24.73
1.475	88.34	87.46	86.53	85.01	83.42	81.12	78.77	74.18	71.41	64.73	54.28	35.58
1.480	91.62	91.01	90.06	89.14	87.96	86.22	84.43	81.01	78.96	73.50	64.82	49.13
1.485	94.76	94.40	93.96	93.24	92.43	91.36	90.18	88.03	86.69	82.94	76.98	64.19
1.490	97.83	97.74	97.58	97.27	96.88	96.54	96.00	95.20	94.63	91.98	89.77	83.52

TABLE IV (*b*)

DERIVED ISOFRACT DATA

C_6H_6 / C_2H_5OH	0 / 100	10.69 / 89.31	21.01 / 78.99	28.94 / 71.06	42.05 / 57.95	52.55 / 47.45	59.26 / 40.74	69.30 / 30.70	78.38 / 21.62	90.28 / 9.72
N_c^{25}	Per cent CCl_4 in ternary									
1.360	4.81	—	—	—	—	—	—	—	—	—
1.365	14.18	—	—	—	—	—	—	—	—	—
1.370	22.47	—	—	—	—	—	—	—	—	—
1.375	30.10	9.81	—	—	—	—	—	—	—	—
1.380	37.18	20.07	—	—	—	—	—	—	—	—
1.385	43.77	29.84	4.91	—	—	—	—	—	—	—
1.390	49.83	38.60	16.87	—	—	—	—	—	—	—
1.395	55.42	45.87	27.58	5.54	—	—	—	—	—	—
1.400	60.66	52.48	37.20	19.39	—	—	—	—	—	—
1.405	65.63	58.54	46.00	31.58	—	—	—	—	—	—
1.410	70.22	64.16	53.88	42.23	—	—	—	—	—	—
1.415	74.43	69.36	60.88	51.48	18.28	—	—	—	—	—
1.420	78.46	74.18	67.53	59.83	34.38	—	—	—	—	—
1.425	82.20	78.68	73.48	67.44	48.58	5.00	—	—	—	—
1.430	85.68	82.88	79.01	74.56	59.99	29.40	—	—	—	—
1.435	89.00	86.83	83.96	80.92	70.08	48.90	12.60	—	—	—
1.440	92.02	90.47	88.48	86.56	79.61	66.24	44.38	—	—	—
1.445	94.83	93.86	92.70	91.63	87.77	80.06	67.84	—	—	—
1.450	97.47	97.03	96.58	96.12	94.48	91.48	87.33	45.90	—	—
1.455	—	—	—	—	—	—	—	—	98.40	99.47
1.460	—	—	—	—	—	—	—	—	17.70	87.17
1.465	—	—	—	—	—	—	—	—	—	72.66
1.470	—	—	—	—	—	—	—	—	—	51.84
1.475	—	—	—	—	—	—	—	—	—	23.07

The angle of intersection of the two sets of iso-lines averages about 60°. Had this angle been close to a right angle, the maximum precision of analysis would have been possible. On the other hand, had this angle been close to 0° (parallel line) or had a double intersection occurred (excessive curvature in

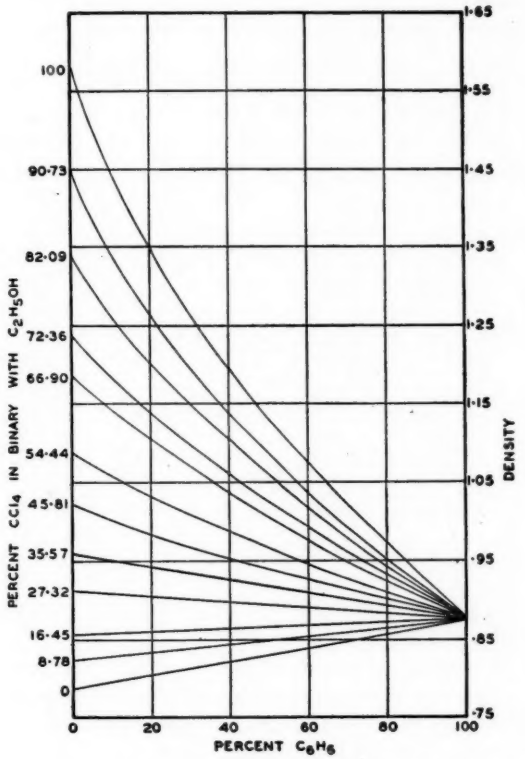

FIG. 3. *Experimental curves*—d_4^{25}.

one set), the analysis would have been impossible. As it is, and using a triangle with sides almost 3 ft. in length, and a criss-cross grid of iso-lines, the analysis is very satisfactory.

The use of the triangular diagram for analysis is simple. Any ternary mixture will have a refractive index and a density lying on the diagram between two isofracts and two isodensity lines. These known properties, lying on interpolated lines, will intersect at a unique point giving the composition of the unknown mixture.

Although we claim only 0.3% accuracy, the analysis is usually better than 0.2% of the total for each component. The following mixtures, weighed out at random, were used to test the attainable accuracy. Compositions obtained

TABLE V

ACCURACY OF THE ANALYTIC DIAGRAM

No.	——	d_4^{25}	N_c	% C_6H_6	% C_2H_5OH	% CCl_4	Maximum deviations, %
1	Weighed		1.45088	71.83	28.17	0	
	Derived			71.85	28.15		0.02
2	Weighed	1.41033		15.20	0	84.80	
	Derived			15.15		84.85	0.05
3	Weighed	1.0610	1.43074	26.32	27.39	46.29	
	Derived			26.3	27.3	46.4	0.11
4	Weighed	0.9124	1.45548	63.77	21.24	14.99	
	Derived			63.8	21.1	15.1	0.15
5	Weighed	0.8824	1.47643	85.07	9.99	4.94	
	Derived			85.1	9.95	4.95	0.03
6	Weighed	1.4425	1.44606	4.37	6.13	89.50	
	Derived			4.2	6.3	89.5	0.17
7	Weighed	1.1859	1.44103	20.50	16.55	62.95	
	Derived			20.70	16.35	62.95	0.20
8	Weighed	0.8413	1.37174	6.03	82.10	11.88	
	Derived			6.2	82.0	11.8	0.17
9	Weighed	0.8108	1.36779	6.08	88.92	5.00	
	Derived			6.3	88.9	4.8	0.22

from the diagram, i.e., from the physical properties, are termed 'derived', as contrasted with the actual or 'weighed' figures.

The analysis is most accurate where the isodensity and isofract lines are close together. In general, where the isodensity lines are widely spread, the isofracts are close together and vice versa. The alcohol corner is the least covered and therefore the least accurate. Analyses in this region will be sensibly affected by errors of 0.00010 unit in either density or refractive index.

Applications

Analysis of Commercial Materials

The use of the analysis diagram for so-called 'practical' or 'stock' materials of industry deserves brief discussion. Table VI lists the properties of commercial materials, together with their deviations from those of the pure materials of this study, while Table VII compares weighed with derived compositions in a single case. The method here is first to find the approximate compositions from the known density and refractive index, assuming that the mixture is of pure components, then to apply a correction to observed density and refractive index, derived from the mixture rule, the deviations of the impure components, and the approximate proportions.

TABLE VI

PROPERTIES OF COMMERCIAL MATERIALS

Component	d_4^{25}	Deviation	N_c^{25}	Deviation
B.D.H. Technical benzene	0.8732	−0.0004	1.49300	−0.00031
Eastman's Practical carbon tetrachloride	1.5848	−0.0004	1.45458	−0.00020
Alcohol (1.7% water)	0.7902	+0.0052	1.35847	−0.00080

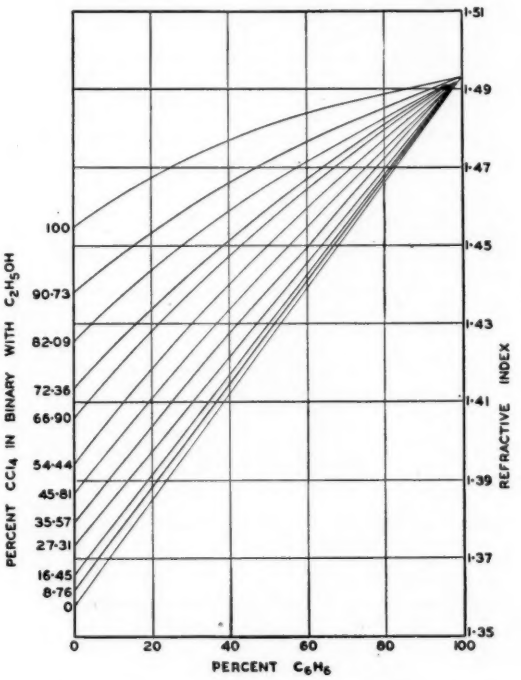

FIG. 4. *Experimental curves—N_c^{25}.*

TABLE VII

ANALYSIS OF A COMMERCIAL MIXTURE

—	d_4^{25}	d_4^{25} (corr.)	N_c^{25}	N_c(corr.)	% C_6H_6	% C_2H_5OH	% CCl_4
Weighed	1.0061		1.45009		45.7	19.9	34.4
Derived		1.0053		1.45046	46.4	19.3	34.3

The maximum error in the above analysis was 0.7%. The error will naturally depend on the purity of the components. Although a thorough survey of every region of the diagram was not made, it is probable that the above materials in ternary mixtures could be analysed to well within 2.0%. This is fair accuracy and industrial application is at least conceivable.

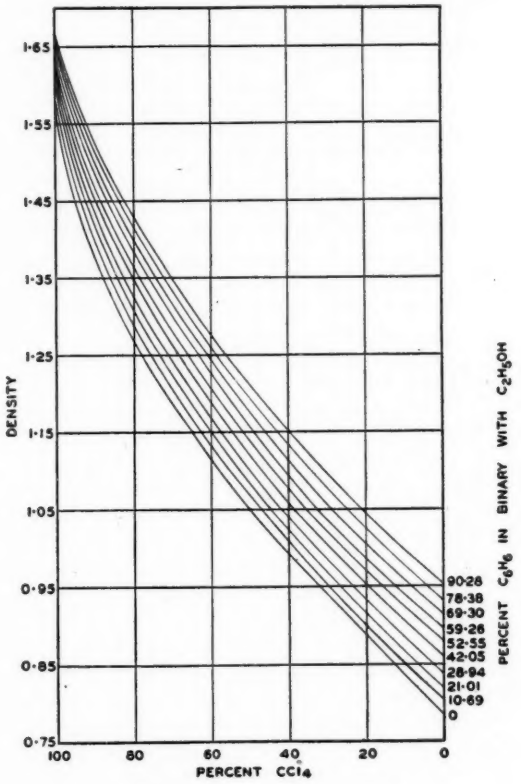

FIG. 5. *Experimental curves—d_4^{25}.*

DEVIATIONS FROM IDEALITY

Experimental curves (Figs. 4 to 7) throw no light on this question, but the maximum on Schreinemakers' vapour surface (19, 20) implies departure from ideality in most of these pseudobinary mixtures. From the results of our work it is possible to calculate approximate changes in specific volume and refractivity on mixing the components. Such calculations have already been made for the binary systems by Hubbard (7, 8), Barbaudy (1), and Hildebrand (6, Chap. V), to mention only a few. Figures for partial vapour pressures and temperature changes on mixing are at least equally important in a discussion

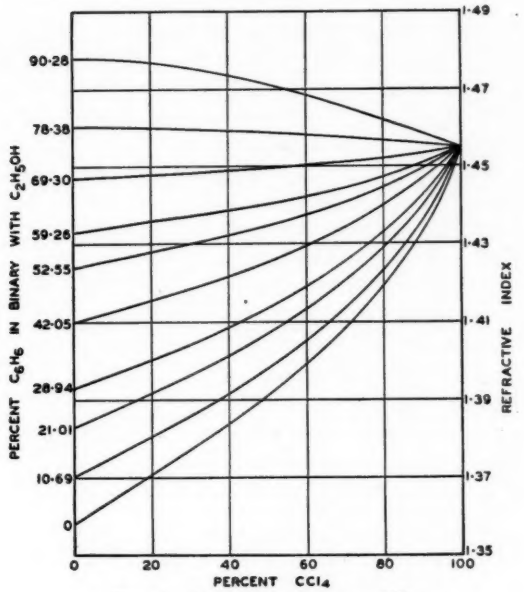

FIG. 6. *Experimental curves—N_c^{25}.*

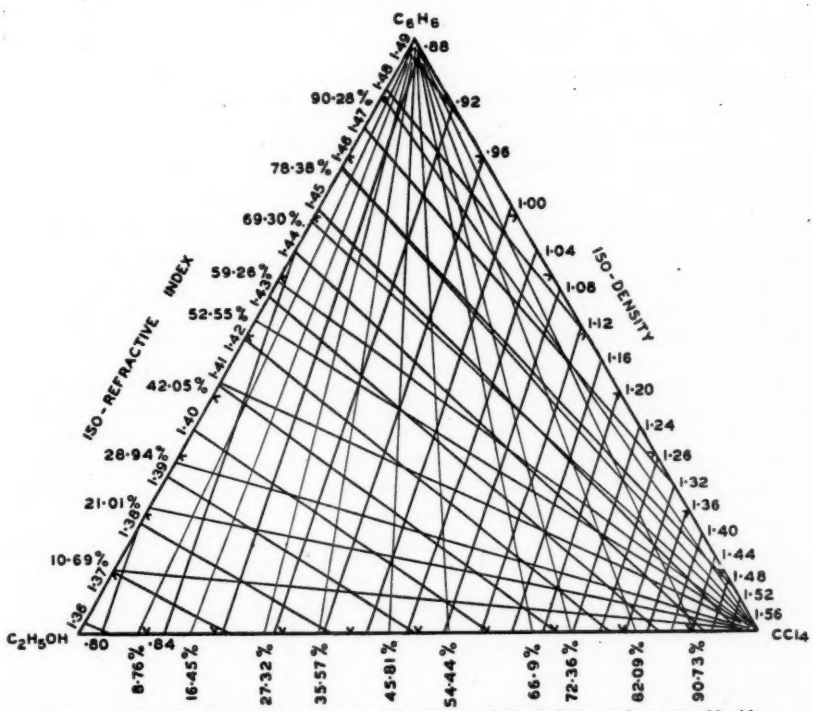

FIG. 7. *Analysis diagram for the system benzene – ethyl alcohol – carbon tetrachloride.*

of non-ideality. Therefore, though we have made calculations of molar volume and specific refractivity for all our systems, we do not reproduce the calculations, since the results are necessarily inconclusive. As far as can be judged on the imperfect basis of our experimental results, the departure from ideality is negligible for all systems except the alcohol–carbon tetrachloride binary, where the departure is still not great. The lack of ternary data on both partial pressures and temperature changes on mixing, however, rule out definite conclusions. Work now in progress will supply the partial pressure data when a more definite conclusion can be reached. Obviously, since most of these pseudobinary mixtures exhibit a maximum on the vapour pressure curve, the solutions cannot be ideal.

Partial molar volumes could be derived in various ways (Lewis and Randall (12)) from our data but they would merely represent a variation of the preceding discussion.

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THE CHROMATES OF SILVER AND COPPER[1]

By A. N. Campbell[2] and H. P. Lemaire[3]

Abstract

At 30° C. silver oxide reacts with an aqueous solution of chromium trioxide to form the normal silver chromate, Ag_2CrO_4, and a limited series of solid solutions of silver chromate in silver dichromate ($Ag_2Cr_2O_7$). The range of solid solubility is approximately 2% in terms of chromium trioxide, and extends from pure silver dichromate towards silver chromate. Both chromates of silver are sparingly soluble in water. No other chromates of silver were found to exist as solid phases at this temperature.

An examination of the system copper oxide – chromium trioxide – water shows that four chromates of copper can form at 30° C. They are: (i) copper dichromate, $CuCr_2O_7 . 2H_2O$, (ii) anhydrous normal copper chromate, $CuCrO_4$, (iii) a simple basic chromate, $CuCrO_4 . Cu(OH)_2$, and (iv) a 2 : 3 basic chromate, $2CuCrO_4 . 3Cu(OH)_2 . H_2O$. These chromates separate from solution in the above order as the chromate concentration is decreased, chromium trioxide itself being the initial solid phase. All four chromates are decomposed (partially) by water.

The solubility curves and ranges of existence have been established in most cases. Copper dichromate has a narrow range of existence, the normal chromate a relatively wide one. In part of this range, however, the chromate is in a metastable state, since it is in equilibrium with solutions that are supersaturated with respect to the simple basic chromate.

Introduction

With a view to establishing the existence and formulae of all the chromates of silver and of copper, systematic study was made of the systems: (i) silver oxide – chromium trioxide – water and (ii) copper oxide – chromium trioxide – water, at 30° C.

In 1906, Schreinemakers (9-13), in a series of papers, described his work on the chromates of the Group 1(*a*) metals. His method of investigation, carried out at 30° C., was the now well-known 'wet residue' method.

A search of the literature revealed that very little work had been done on the chromates of the Group 1 (*b*) metals, possibly because the chromates of the heavy metals are relatively insoluble and correspondingly more difficult to work with. The systematic investigation of the system silver oxide – chromium trioxide – water had never been undertaken. The system copper oxide – chromium trioxide – water had, however, been partially examined by Hayek (6) in 1934. His method was that of conductimetric measurements, not the solubility method, and his investigation was restricted to the basic region.

The object of this work was to complete the study of the Group 1 chromates by investigating those of silver, copper, and gold. Lack of time restricted the investigation to silver and copper, but, in any case, it is doubtful whether gold forms a chromate.

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The Group 1(*a*) metals, according to Schreinemakers (9), form the following chromates, stable as solid phases at 30° C.

TABLE I

CHROMATES OF THE ALKALI METALS

Lithium	Sodium	Potassium	Rubidium	Caesium
$Li_2CrO_4 . 2H_2O$	Na_2CrO_4	K_2CrO_4	Rb_2CrO_4	Cs_2CrO_4
$Li_2Cr_2O_7 . 2H_2O$	$Na_4CrO_5 . 13H_2O$	$K_2Cr_2O_7$	$Rb_2Cr_2O_7$	$Cs_2Cr_2O_7$
	$Na_2CrO_4 . 4H_2O$	$K_2Cr_3O_{10}$	$Rb_2Cr_3O_{10}$	$Cs_2Cr_3O_{10}$
	$Na_2Cr_2O_7 . 2H_2O$	$K_2Cr_4O_{13}$	$Rb_2Cr_4O_{13}$	$Cs_2Cr_4O_{13}$
	$Na_2Cr_3O_{10} . H_2O$			
	$Na_2Cr_4O_{13} . 4H_2O$			

All the chromates of sodium and lithium, except the normal chromate of sodium, are hydrated, while none of the chromates of potassium, rubidium, or caesium contain water of crystallization. Only the lower chromates of potassium, rubidium, and caesium are stable in pure water; the tri- and tetra-chromates decompose (partially) into lower chromates on entering solution. All these chromates are quite soluble in water.

The present investigation has shown that the analogy between the chromates of Group 1(*a*) and those of Group 1(*b*) is not close. Silver forms two chromates both of which are sparingly soluble in water at 30° C., while copper forms several chromates all of which are more soluble than those of silver, but not nearly as soluble as those of the Group 1 (*a*) metals. All the copper chromates are hydrated except the normal salt. In this respect the copper chromates resemble the sodium chromates, but no copper chromates above the dichromate were found. Another point of difference is that all the chromates of copper are unstable with respect to pure water.

The System: Silver Oxide – Chromium Trioxide – Water

Only the normal chromate and the dichromate of silver are known. Silver chromate can be prepared in various ways. Most of these involve the use of potassium chromate and a soluble salt of silver, usually the nitrate. It can also be prepared by the action of potassium chromate on silver oxide (4). Silver dichromate is prepared in much the same way, but with less difficulty. According to Moser (8), the action of chromic acid on a solution of silver nitrate furnishes crystals of silver dichromate, $Ag_2Cr_2O_7$. It can also be obtained by adding potassium dichromate to a solution of silver salt.

Silver chromate crystallizes in various colours, depending on the mode of preparation. There are two common forms; (*a*) the red-brown (varying from

orange to deep reddish brown), and (*b*) the green (varying from dark green to greenish black, but red in transmitted light). It has now been proved (17) that the red and green silver chromates are identical in structure, the difference in colour being due to grain size only. In our work, only the red variety was obtained. The solubility at 30° C. is 2.9 mgm. per 100 gm. water (16).

Silver dichromate forms crystals that are dark brown or grey by reflected light and scarlet red by transmitted light (19). When boiled with water it forms the dark green chromate and an acid solution that deposits dichromate on cooling:

$$Ag_2Cr_2O_7 + H_2O = Ag_2CrO_4 + H_2CrO_4$$

Sherill (16) gives the solubility at 25° as 7.3×10^{-3} mole per litre.

Experimental

Preparation of Materials

Silver Oxide.—Silver oxide, Ag_2O, was prepared from silver nitrate and sodium hydroxide. A weak 5% sodium hydroxide solution was slowly added, in slight excess, to a 25% silver nitrate solution. The dark brown precipitate was washed several times with both hot and cold water and placed in a desiccator over water. Mellor (7, p. 372) states that silver oxide prepared in this way contains 1 or 2% silver hydroxide and probably traces of silver carbonate. Since silver oxide decomposes on drying, it was impossible to investigate the purity of the oxide by direct analysis. In any case, the presence of silver hydroxide would not alter the behaviour of the system.

Chromium Trioxide.—The chromium trioxide used was a British Drug Houses product of 99.87% purity.

Water.—The water was twice distilled and had a conductivity not greater than 10^{-5} mhos.

Methods of Analysis

The standard potassium thiocyanate method (Volhard's method) was employed to determine silver. The presence of chromate ion, however, presented a difficulty in determining the end-point. The usual end-point is obscured by the orange colour of the chromate ion and this difficulty increases with increasing concentration of chromate. It was therefore necessary to reduce the chromate ion to chromic ion by adding a small amount of sodium stannite. The colour was thereby changed from its original orange to a greenish-blue. The colour change at the end-point was then from blue to brown. The end-point was clearly indicated by a sudden darkening of the solution when one drop of potassium thiocyanate was added in excess. The accuracy of the method was checked by adding potassium dichromate solution to a solution of known silver content and then adding sodium stannite till the colour of the solution turned to a light blue. The solution was then analysed by the method described above, whereupon the analytical determination agreed with the known amount of silver.

Determination of chromate ion was carried out by the standard method of reducing the chromate with ferrous salt (15). The sample for analysis was dissolved in dilute sulphuric acid, not hydrochloric acid, so that the back titration could be performed with potassium permanganate instead of potassium dichromate.

Apparatus and Experimental Procedure

The thermostat operated at a temperature of 29.92° ± 0.03° C. The initial quantities of material were in each case 100 cc. water and 10 gm. wet silver oxide. Increasing quantities of chromium trioxide were added in successive trials to the above quantities of water and silver oxide.

To ensure attainment of equilibrium, conductimetric measurements were made daily on the mixtures, which were stirred constantly. These measurements also provided a measure of the rate of attainment of equilibrium. It

TABLE II

SOLUBILITY DATA IN THE SYSTEM $Ag_2O - CrO_3 - H_2O$ AT 29.9° C.

Sample No.	Wt. CrO_3	Time of stirring, days	Nature of solid phase	Specific conductivity, mhos	Analysis, % liquid phase and wet solid phase, respectively			
					Liquid phase		Wet solid phase	
					Ag_2O	CrO_3	Ag_2O	CrO_3
1	0.5 gm	3	Silver oxide and silver chromate	1.76×10^{-4}	Trace	—	55.2	4.01
2	1.0	3	" "	1.69×10^{-4}	Trace	—	52.4	8.93
3	1.5	3	" "	2.09×10^{-4}	Trace	—	30.2	6.76
4	2.0	3	" "	4.13×10^{-4}	Trace	—	51.2	15.3
5	2.5	3	" "	8.28×10^{-4}	Trace	—	51.9	18.9
6	3.0	4	Silver chromate and solid solution	5.82×10^{-3}	0.09	0.21	50.6	25.1
7	3.5	5	" "	5.93×10^{-3}	0.08	0.21	52.9	26.5
8	4.0	4	" "	5.20×10^{-3}	0.11	0.19	49.9	29.4
9	5.0	6	" "	5.01×10^{-3}	0.10	0.18	45.6	34.1
10	6.0	8	Solid solution	1.11×10^{-2}	0.07	0.34	44.7	35.5
11	8.0	—	" "	3.81×10^{-2}	0.08	2.55	44.3	35.7
12	10	5	" "	6.04×10^{-2}	0.1	4.07	43.4	35.8
13	14	21	" "	9.32×10^{-2}	0.1	7.11	46.2	38.6
14	15	6	" "	8.56×10^{-2}	0.1	8.11	44.3	38.1
15	25	8	" "	1.07×10^{-1}	0.1	15.4	40.7	38.4
							40.8	37.7
16	40	8	" "	1.00×10^{-1}	0.1	24.0	38.4	39.1
						23.9	38.7	39.4
17	70	6	" "	—	0.1	35.1	42.4	43.4
							37.5	42.4
18	100	8	" "	—	0.1	46.9	40.9	46.1
						47.0	38.1	46.0
19	130	8	" "	—	0.1	53.5	40.4	47.7
						53.6	37.8	48.2
20	170	8	" "	—	0.1	58.5	39.8	49.5
						58.9	36.0	50.3
21	190	8	Silver dichromate and CrO_3	—	0.1	61.9	31.3	57.0
						62.0	29.4	57.3
22	200	8	Silver dichromate and CrO_3	—	0.1	61.9	23.5	64.3
						61.9	24.9	64.6

will be shown in the discussion of results that the conductimetric method is not always sensitive enough, and then a false equilibrium, slightly removed from the true equilibrium, sometimes results.

The resistance of samples of low conductivity was considerably affected by gaseous impurities derived from the air of the laboratory. To compensate for this error, a blank containing distilled water only was kept in the thermostat with the sample under investigation. The conductivity of the blank was subtracted from the conductivity of the test sample. Solutions containing more than 40 gm. of chromium trioxide per 100 gm. of water had a very high conductivity and it was impossible to make resistance measurements of any useful accuracy on these samples.

The filtration apparatus was of the standard type. It included a ground glass filter with a tube connecting it to the filtrate bottle which, in turn, was attached to the filter pump. The analyses were frequently made in duplicate.

Results

Table II contains the analyses of liquid phases and equilibrium wet solid phases, as well as the conductivity data. The equilibrium data are plotted in Fig. 1 in weight per cent.

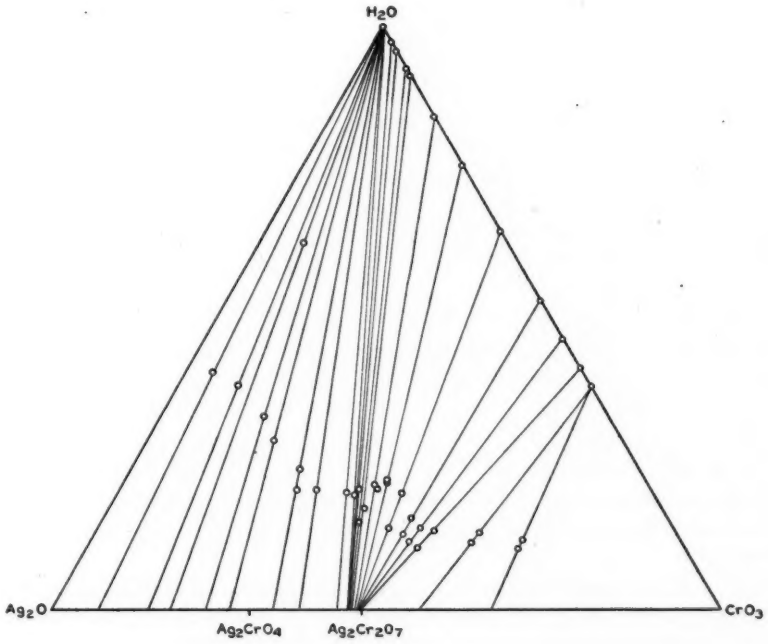

Fig. 1.

Discussion of Results

Because of the very low solubility of silver oxide and the chromates of silver, Fig. 1 gives no information as to the formation of normal silver chromate at 30° C., but its existence is clearly shown in Figs. 2 and 3. In Fig. 2 the initial quantity of chromium trioxide in the sample is plotted as abscissa and the percentage of chromium trioxide in solution as ordinate. In Fig. 3 the total amount of chromium trioxide is again plotted as abscissa, and the conductivity of solution as ordinate.

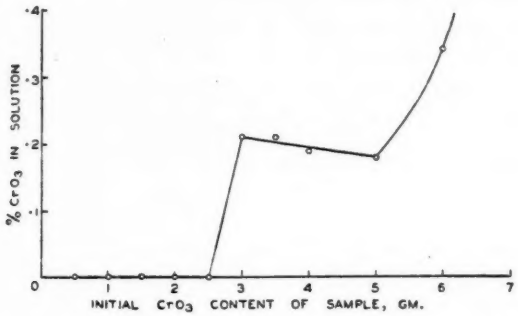

FIG. 2.

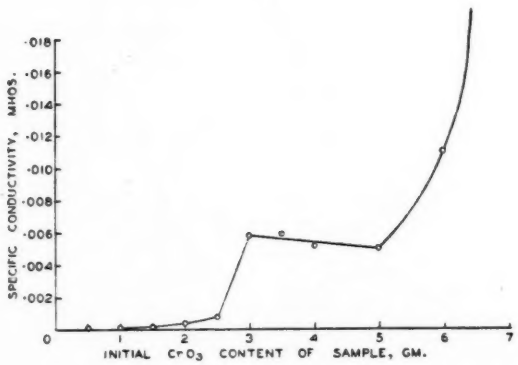

FIG. 3.

In a system of three components, two solid phases in equilibrium with solution constitute an isothermally invariant system. The composition of the solution therefore remains constant until one or other of the solid phases disappears.

The wet silver oxide employed in this work contained 65.4% silver oxide. The amount of chromium trioxide necessary to convert completely 10 gm. of the wet oxide to silver chromate, Ag_2CrO_4, is therefore 2.8 gm. Figs. 2 and 3 indicate that samples containing 0.5 to 2.5 gm. chromium trioxide

give rise to a liquid phase of constant composition and the same is true of samples containing 3.0 to 5.0 gm. chromium trioxide. In the 2.5 to 3.0 gm. range both the chromium trioxide in solution and the conductivity jump suddenly to a higher constant value. This indicates that in this range one solid phase, the oxide, disappears and the system gains one degree of freedom.

The first heterogeneous solid mixture is therefore composed of silver oxide and silver chromate. When enough chromium trioxide has been added to convert all the oxide to the chromate (2.8 gm.) the system becomes for a short range of concentration isothermally univariant, i.e., the composition of the saturated solution changes, but it soon attains a second constant value because a new compound appears, making the solid system once more heterogeneous, i.e., it is now a mixture of silver chromate and of saturated solid solution of silver chromate in silver dichromate. The limit of solid solubility is indicated in Figs. 2 and 3 by a break in the curve when the total chromium trioxide content of the sample is 5 gm. After this point the system is isothermally univariant and the curve rises very rapidly as chromium trioxide builds up in solution.

The range of solid solution as determined from Fig. 1, is about 2% chromium trioxide, one limit being pure dichromate and the other solid solution of chromate in dichromate: it is impossible to say, because of the low solubility of silver chromate, whether there is a corresponding solid solubility of dichromate in chromate; the conductivity method is not sufficiently sensitive to answer the question either.

The departure from ideal behaviour in Figs. 2 and 3, e.g., 'horizontals' not truly horizontal, is due to the fact that in these sparingly soluble systems equilibrium is approached very slowly. The conductivity is at first high when the chromium trioxide is added and then falls off asymptotically with time, as the dissolved chromium trioxide is converted to 'insoluble' chromate. It is thus very natural that solutions were sometimes taken to be equilibrium solutions which were not really so. The difference in the analytical results is, however, negligible.

The heterogeneous mixture of silver oxide and silver chromate was dark brown while the heterogeneous mixture of silver chromate and saturated solid solution was of a more reddish shade. Both mixtures appeared as blood red crystals in transmitted light under the microscope.

The System: Copper Oxide - Chromium Trioxide - Water

Four chromates of copper are described in the literature:— copper dichromate, normal copper chromate, and two basic copper chromates, the compositions of which are in doubt.

Copper dichromate crystals were first isolated by Droege (3) in 1857. He assigned to the compound the formula $CuCr_2O_7 . 2H_2O$. J. Schulze (14) and M. Gröger (5) also succeeded in isolating crystals of this composition by the action of chromium trioxide solution on copper carbonate. Gröger

also claims the existence of anhydrous copper dichromate and of a compound $CuCr_4O_{13} \cdot 2H_2O$. This is the only occasion on which a higher chromate than the dichromate is claimed to exist.

The copper dichromate crystals are described in the literature as blackish-brown in colour, but those obtained by us were usually a bright wine-red, but in the presence of a large amount of adhering mother liquor their colour seemed much darker.

All investigators, except one, claim that the normal chromate is anhydrous. Briggs (2) assigns to this salt the formula $CuCrO_4 \cdot 2H_2O$, but our systematic investigation shows that the normal chromate is anhydrous.

There is, or has been, considerable controversy regarding the composition of the basic chromates of copper. Copper trioxychromate ($CuCrO_4 \cdot 3Cu(OH)_2$) is said to be produced by the action of an excess of an alkaline solution of potassium chromate on a solution of copper sulphate, but according to Schulze (14) and Gröger (5), the chromate formed in this way is the dioxychromate ($CuCrO_4 \cdot 2Cu(OH)_2$).

The only systematic investigation of the system copper oxide – chromium trioxide – water is that of Hayek (6) in 1934. His work, carried out at 40° C., showed the existence of two basic chromates, viz., $2CuCrO_4 \cdot 3Cu(OH)_2 \cdot H_2O$ and $CuCrO_4 \cdot Cu(OH)_2$. Hayek's experimental procedure consisted in stirring various proportions of copper oxide and chromium trioxide in 100 cc. of water till constant conductivity was attained, i.e., essentially the same method as we used in the investigation of the silver chromates. The yellowish-brown 3 : 3 basic chromate formed even at the greatest dilutions. This salt corresponds to the dioxychromate, $CuCrO_4 \cdot 2Cu(OH)_2$, obtained by previous workers, and Hayek believes that the greater proportion of base in the dioxychromate results from the decomposition by boiling of the 3 : 2 basic salt, which is not stable in hot water.

The simple basic salt, $CuCrO_4 \cdot Cu(OH)_2$, occurs in two forms—a copper red and a chocolate brown to lilac form. This is probably the brownish precipitate mentioned by Gröger (5), which deposits previous to the formation of the lower chromate. Hayek found that boiling the simple basic chromate with water results in the formation of a yellow salt, but he does not attribute the change in colour to a change in composition but to a change in superficial colouring, the brown appearance being caused by a superficial layer of chromic acid and the yellow colour by a layer of hydroxyl ions or $Cu(OH)_2$ molecules.

Although our investigation is restricted mostly to the acid region, the few experiments conducted in the basic region have yielded results in conformity with those of Hayek.

Experimental

Preparation of Copper Oxide

The method by which the copper oxide was prepared was found to have considerable influence on the progress of the work. The copper oxide of commerce, which has no doubt been ignited, fails to react to any appreciable

extent with chromium trioxide. Our attempts to prepare pure copper oxide by the action of sodium hydroxide on copper sulphate failed, because it is very difficult to remove all the sulphate from the copper oxide by washing. We finally succeeded by using the method of Vogel and Reischauer (18). According to this method, a neutral solution of copper nitrate is divided into two equal parts. To one half, concentrated ammonia is added until the precipitated copper hydroxide redissolves. This portion is then added slowly to the other half and the mixture boiled under reflux for four hours; the copper hydroxide which forms at first is thus converted to copper oxide. The oxide is filtered hot and washed twice with hot water and once with cold. To remove the final traces of nitrate, the copper oxide is boiled under reflux for another three hours, and again washed several times with hot and cold water till the oxide is free from nitrate.

Method of Analysis

Chromate was determined as described under the chromates of silver. Copper was determined electrolytically. For solutions containing high chromate concentrations, the copper was checked gravimetrically as cuprous sulphide. The high concentration of chromate was found not to interfere with the electrolytic determination.

Results

The analytical results are contained in Table III, and are plotted in Fig. 4, in weight per cent.

Discussion of Results

Time of stirring was the most important factor in this work. Depending on the nature of the solid phase, some samples took only a short time to attain equilibrium while others were extremely sluggish in their behaviour. In samples in which chromium trioxide was the solid phase, equilibrium was established relatively quickly in two or three days. With copper dichromate as solid phase, two weeks were necessary, while with copper chromate a month was required. When the stirring was not carried on for a sufficient length of time, the action on the copper oxide was incomplete. In general, the time required to attain equilibrium increased with decreasing chromate concentration in solution.

Five different solid phases may be in equilibrium with solution, depending on the chromate concentration, viz.:— (i) chromium trioxide, CrO_3 ; (ii) copper dichromate, $CuCr_2O_7 . 2H_2O$; (iii) anhydrous normal copper chromate, $CuCrO_4$; (iv) simple basic chromate, $CuCrO_4 . Cu(OH)_2$; (v) 2 : 3 basic chromate, $2\ CuCrO_4 . 3Cu(OH)_2 . H_2O$.

Straight lines joining the composition of the solid phases to the apex of the triangle of the equilibrium diagram do not intersect the respective solubility curves. All four chromates, therefore, decompose partially (are incongruently soluble) when brought into contact with pure water.

TABLE III

SOLUBILITY DATA IN THE SYSTEM $CuO - CrO_3 - H_2O$ AT 29.9° C.

Sample No.	Time of stirring	Nature of solid phase	Analysis, % liquid phase and wet solid phase, respectively			
			Liquid phase		Wet solid phase	
			CuO	CrO_3	CuO	CrO_3
1	2 days	CrO_3	—	64.8	—	100
2	3 "	"	1.0	64.4	Trace	97.4
3	3 "	"	5.7	62.1	0.9	95.0
4	3 "	"	10.9	60.6	1.11	96.3
5	3 "	"	12.6	61.0	2.76	93.8
6	2 weeks	$CuCr_2O_7 . 2H_2O$ and CrO_3	13.2	61.8	19.7	64.9
7	2 "	" "	13.1	61.7	14.5	72.4
					20.3	62.6
8	2 "	$CuCr_2O_7 . 2H_2O$	13.8	60.7	20.8	62.8
9	2 "	"	14.6	58.6	20.4	61.0
					22.0	60.4
10	2 "	"	15.0	54.7	22.0	60.4
11	4 "	$CuCrO_4$	14.5	53.1	28.2	54.0
12	4 "	"	15.1	47.4	28.7	51.1
					26.1	50.0
13	4 "	"	15.4	46.9	27.6	50.1
14	4 "	"	15.0	40.5	26.3	45.8
15	2 "	"	12.7	31.9	25.1	41.0
					23.7	37.5
16	2 "	"	10.1	25.4	21.1	34.7
17	2 "	"	8.80	22.3	23.1	35.9
18	1 "	"	7.94	19.6	29.3	40.4
19	1 "	"	6.60	16.6	27.6	38.0
20	1 "	"	5.80	14.8	21.6	30.4
21	1 "	"	4.31	11.3	29.0	38.6
					22.9	30.8
22	5 days	$CuCrO_4 . Cu(OH)_2$	6.80	10.5	23.0	31.2
23	5 "	"	5.70	8.53	35.6	24.8
24	5 "	$2CuCrO_4 . 3Cu(OH)_2 . H_2O$	4.74	7.31	31.0	18.2
			4.74	7.32	30.7	17.9
25	5 "	"	2.40	5.88	31.7	18.6
			2.42	5.89	30.3	18.3

Only a few experiments were made in the region of basic salt. The few results obtained are in accordance with the findings of Hayek (6), viz., simple basic chromate, $CuCrO_4 . Cu(OH)_2$, and 2 : 3 basic chromate, $2CuCrO_4 . 3Cu(OH)_2 . H_2O$. Both the basic chromates are yellow, the normal chromate forms dark-yellow crystals in the dilute region and brownish-red ones in the more concentrated region, while the dichromate crystallizes in bright red-wine needles.

Only one invariant point was established experimentally, viz., the chromium trioxide – copper dichromate invariant. The invariant for which the solid phases are normal chromate and dichromate should be realizable but it was not established in this investigation. It has been narrowed down, however, to a very small range of concentration. The solubilities of the basic chromates are so small that the intersection of their respective solubility curves at invariance is not detectable.

The solubility curves of the simple basic chromate and the normal chromate do not intersect. For some undetermined region of concentration, therefore, the normal copper chromate must be in a metastable state. The reason for lack of definiteness in the data here is the very great slowness with which true equilibrium is attained in the solutions containing less chromate.

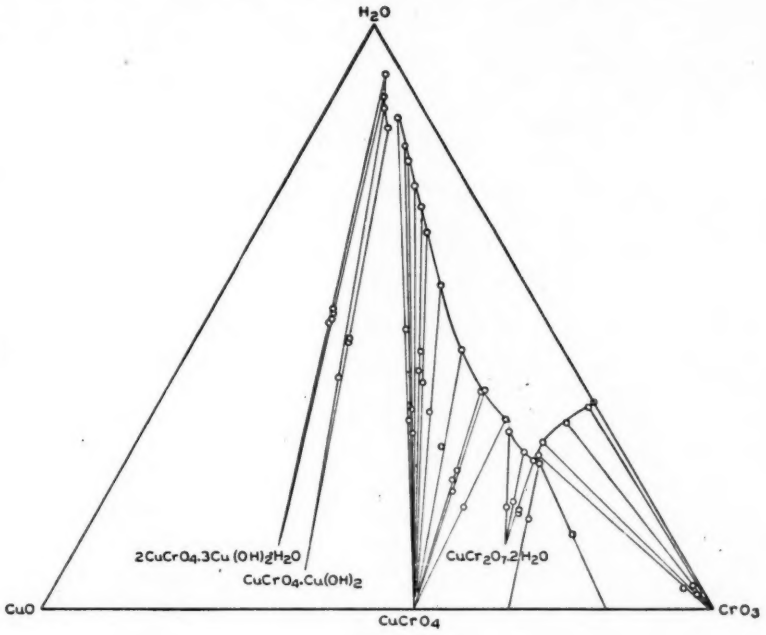

FIG. 4.

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THE DETERMINATION OF PARTICLE SIZE BY LIGHT SCATTERING[1]

By J. Bardwell[2] and C. Sivertz[3]

Abstract

A critical study has been made of the various observations necessary for the determination of the size of small dielectric particles by the Debye–Einstein equation, which can take the form:

$$\text{Mass of particle} = \frac{3}{32\pi^3}\frac{\lambda^4}{\mu_0^2}\left(\frac{d\tau}{dc}\right)_{c=0}\Big/\left(\frac{d\mu}{dc}\right)^2.$$

The turbidity measurements were made with a Beckman spectrophotometer and those of refractive index with a Zeiss dipping refractometer. This article deals especially with the determination of the turbidity and refractive index gradients. The method was applied to the determination of latex particle size and gave results in good agreement with independent methods.

Introduction

Methods for the determination of the size of particles of colloidal dimensions have in recent years become of increasing importance. Much of this new interest has arisen from the wide field of observation opened up by the development of the ultracentrifuge and the electron microscope. However, the application of these techniques is greatly limited by their availability, and to some extent by the conditions of observation that must be met. Consequently, a relatively simple technique for particle size determination involving light-scattering measurements may be expected to find wide application and interest. It is the object of this paper to present a detailed account of the application of such a technique based upon the theoretical work of Einstein (2) and Debye (1), in the belief that this technique constitutes a powerful tool in the hands of research workers.

For example, during the preparation of this paper on the particle size of synthetic latex, G. Oster (5) described a similar method for the determination of the molecular weight of certain viruses.

While the method described below is a very welcome addition to the relatively few absolute methods of size determination, it has certain limitations, chief of which is its restriction to sizes that are small relative to the wavelength of the light scattered. Nevertheless, there remains a large region of particle sizes to which the method may be applied.

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Theoretical

Debye's (1) modification of Einstein's equation for critical opalescence results in the following expression for the turbidity of solutions:

$$\tau = \frac{8\pi^3}{3}\frac{kT}{\lambda^4}\frac{\left(c\frac{d\epsilon}{dc}\right)^2}{c\left(\frac{dP}{dc}\right)}, \tag{1}$$

where the turbidity, $\tau = 2.303\ D$, and D is the optical density of a solution of unit length.

ϵ = optical dielectric constant = μ^2 for non-absorbing systems,

μ = the refractive index at wave-length λ,

P = osmotic pressure,

c = number of grams per cubic centimetre of solute.

An analysis of the variables in Equation (1) reveals that τ, c, μ, T, and λ are all capable of direct measurement and consequently it is the *osmotic pressure gradient that this equation does in fact evaluate.* Now, osmotic pressure may be adequately expressed by an equation of the form

$$P = kT\left[\frac{c}{m} + A_2c^2 + A_3c^3 + \ldots\right], \tag{2}$$

where A_2 is the second virial coefficient and m is the mass of the particle. Introducing the value of the derivative $\frac{dP}{dc}$ from Equation (2) in Equation (1) (neglecting higher than squared terms), and the differential $d\epsilon$ as $2\mu\, d\mu$, yields,

$$\tau = \frac{32\pi^3}{3\lambda^4}\cdot\frac{\mu_0^2\left(\frac{d\mu}{dc}\right)^2 c\cdot m}{\{1 + 2A_2mc\}}. \tag{3}$$

Since the refractive index, μ, of the entire sol at low concentration differs only slightly from μ_0, the refractive index of the medium, the latter is conveniently used in place of the former in Equation (3).

Now the mass of the particle m that is implicit in Equation (3) may be expressed either as a function of τ/c; i.e.

$$m = \frac{3\lambda^4}{32\pi^3}\frac{\tau/c\ (1 + 2A_2mc)}{\mu_0^2\left(\frac{d\mu}{dc}\right)^2}, \tag{4}$$

or in terms of the specific turbidity $\left(\frac{d\tau}{dc}\right)$ obtained by differentiating Equation (3), i.e.,

$$m = \frac{3\lambda^4}{32\pi^3}\frac{\left(\frac{d\tau}{dc}\right)(1 + 2A_2mc)^2}{\mu_0^2\left(\frac{d\mu}{dc}\right)^2}. \tag{5}$$

Equations (4) and (5) are true for all values of c for which the osmotic pressure equation holds. They are of interest to show how deviations from the Van't Hoff equation for osmotic pressure might be expected to influence the determination of particle mass. In practice the observed values of τ/c are extrapolated to $c = 0$, where of necessity $\underset{c=0}{\text{Lim}} \frac{\tau}{c} = \underset{c=0}{\text{Lim}} \frac{d\tau}{dc}$.

Equations (4) and (5) form the basis of calculations of m and A_2 from experimental measurements of concentration, turbidity, and refractive index at a definite wave-length.

Experimental

(a) Measurement of Turbidity

Measurements of turbidity have been widely used (6) in quantitative analysis to estimate the concentration of dispersed material, on the assumption of similar particle size. Equation (3) indicates that size can be *evaluated* by measurement of both concentration and turbidity at a known wave-length.

Implicit in the above theory is the assumption of symmetrical distribution of the scattered radiation. This exists provided the particle diameter, d, is small compared to the wave-length. ($d = \frac{\lambda}{20}$ or less.) For particles of diameter comparable to the wave-length, phase differences result in dissymmetry in the scattered radiation with more forward than backward scattering (Mie effect) (4). Consequently when $d > \lambda/20$ the calculated values of size are smaller than the true values. However, a correction can be applied, which amounts to less than 5% for the sizes studied in this case, namely, up to 1000 Å.

The Beckman spectrophotometer was chosen for light-scattering measurements since it readily provides a precise and absolute value of the turbidity as defined above. The monochromator provides an accurately calibrated beam of essentially monochromatic light (band width 5 to 20 Å) over a large range of the spectrum (2200 to 10,000 Å) and so the instrument is also suitable for the measurement of wave-length exponent. In the transmittance region of 6 to 97% the precision is 0.1 to 0.5%.

Since measurements of apparent absorption are substituted for measurements of scattering it is important that the 'consumptive' absorption of the dispersed material be negligible compared to the 'conservative' absorption. That this condition is fulfilled in the case of latex is indicated by the close adherence for all wave-lengths to the inverse nth power of wave-length in the measured turbidity (Fig. 1). Even if this were not the case, a wave-length could be found to minimize the effect of consumptive absorption. This flexibility is one of the advantages of the use of such a spectrophotometer.

Fig. 1 shows the results of measurements, in the region 3200 to 10,000 Å, of the turbidity of a series of concentrations of GR-S latex. The average particle diameter of this latex was 940 Å. A study of Fig. 1 reveals the following characteristics.

(1) Linearity of log D vs. log λ over a large range of wave-length for all concentrations. The slopes of the linear regions are found to lie close to the average value of 3.45.

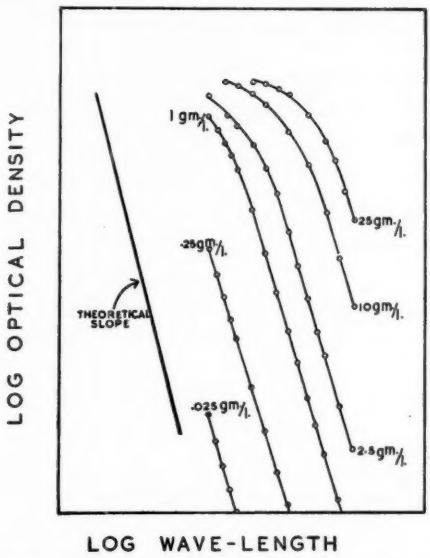

FIG. 1. *The turbidity of solutions of small dielectric particles (latex) as a function of wave-length.*

(2) Above an optical density of 1.2 there is a marked decrease in the value of the wave-length exponent (slope) for all concentrations. This is believed to be due to the effect of diffusion of light caused by secondary scattering.

If Equation (1) is generalized to $\tau = A\,\lambda^n$ we find at least three reasons for deviation of $-n$ as measured, from the theoretical value of 4. The effect of secondary scattering is a decrease in the value of $-n$ from the theoretical. The dispersion of refractive index with wave-length as approximated by the Cauchy equation,

$$\mu = a + \frac{b}{\lambda^2},$$

predicts a value of $-n > 4$.

The major reason for the observed value of $-n = 3.45$ is, however, the fact that the particles are somewhat too large for symmetrical scattering except at the longest wave-lengths used. Similar measurements with particles of diameter 1500 Å gave a value of $-n = 2.5$. This suggests another method of particle size estimation in a certain range, namely, the variation of wave-length exponent. A study of this has recently been made by Dr. W. Heller (3).

When a satisfactory theory relating the wave-length exponent to particle size and shape is evolved, it should provide a convenient method for the

determination of these latter properties. In the absence of such theory no extensive experimentation was carried out in this study.

In the case of a sol of unknown particle size it is desirable to have qualitative knowledge of the ratio of d/λ. This may readily be obtained by measurement of the wave-length exponent. In our experience, for wave-length exponent values higher than three, the method is subject to no serious error.

Constant wave-length sections of the family of curves in Fig. 1 are shown in Fig. 2. Deviations from linearity are noted in all cases, especially at the larger values of both turbidity and concentration. These effects result from secondary scattering and the deviations from ideal osmotic behaviour described in Equation (2).

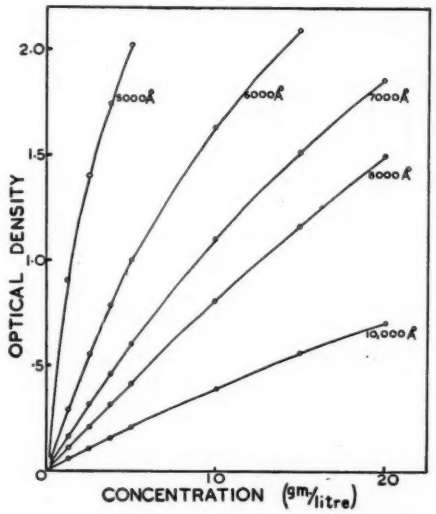

FIG. 2. *Turbidity as a function of concentration.*

Two methods have been employed in this work to obviate the complexities referred to in the preceding paragraphs.

First Method: Use of a Combination of Wave-lengths

Equation (4) may be written as follows for the region $c \doteq 0$,

$$M = \frac{4.22 \times 10^{21}}{\mu_0^2 \left(\frac{d\mu}{dc}\right)^2} \cdot \frac{D\lambda^4}{c}, \tag{6}$$

where M is the mole weight of the light scattering material, i.e., Avogadro's number times the m of Equation (4). It is worth noting that a simultaneous knowledge of M, the mole weight of the latex particle, and $\overline{M}$, the average molecular weight of the *polymer molecule* of which the former is composed,

will at once reveal the number of average polymer molecules contained in an average latex particle. This amounts to about 1000 molecules per latex particle for the largest particles found in this study.

Since for small particles the wave-length exponent approaches 4, the value of $D\lambda^4$ may be obtained as the slope of the D vs. λ^{-4} plot as shown in Fig. 3. Extrapolation of the derived values of $\frac{D\lambda^4}{c}$ to zero concentration eliminates the effect of both secondary scattering and the higher terms in Equation (2).

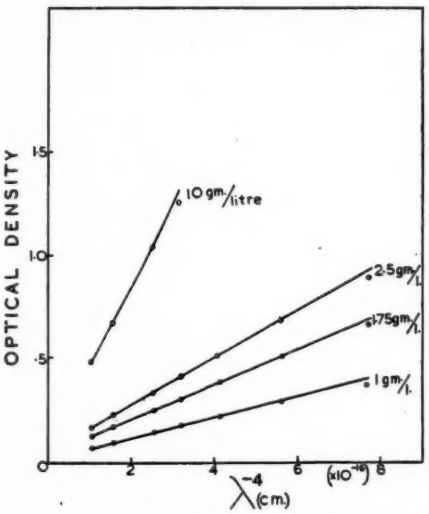

FIG. 3. *Turbidity as a function of inverse fourth power of wave-length.*

The only measurements now remaining for the calculation of M are those of μ_0 and $\frac{d\mu}{dc}$, which are further discussed below.

The equivalent of this method was recently reported in connection with the determination of the molecular weights of viruses (5). It is to be noted that this method requires dispersion corrections of μ_0 and $\frac{d\mu}{dc}$ (neglected in Reference (5)) to the appropriate wave-lengths, and since these involve some uncertainties the following method was chosen instead.

Second Method: Use of a Single Wave-length

Because the refractive index as measured by commercial refractometers is for $\lambda = 5893$ Å, this wave-length was chosen for scattering measurements. In general this allows use of concentrations of the same order of magnitude for both light scattering and refractive index. The refractive index μ_0 of the medium for the latex systems studied was found to be 1.33. Use of these

numerical values of λ and μ, and expressing m as the mole weight, Equation (5), in the limit of zero concentration, becomes

$$M = 28450 \cdot \frac{\left(\frac{dD}{dc}\right)_0}{\left(\frac{d\mu}{dc}\right)^2}, \tag{5}$$

where $\frac{d\mu}{dc}$ = specific refractive index and $\left(\frac{dD}{dc}\right)_0$ = specific optical density obtained by extrapolation of measured values of $\frac{D}{c}$ to zero concentration or to zero turbidity. It was found convenient to prepare the required solutions

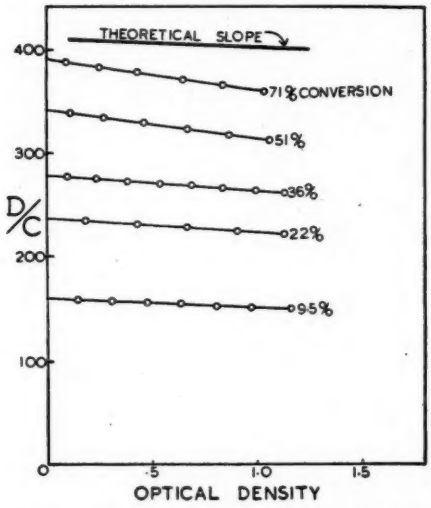

FIG. 4. *Extrapolation of the turbidity gradient to infinite dilution.*

by successive addition of aliquot portions of concentrated polymer solution to the solvent. (Fig. 4 indicates the extrapolation for a series of GR-S latices of increasing conversion.)

(*b*) MEASUREMENT OF $\frac{d\mu}{dc}$, THE SPECIFIC REFRACTIVE INDEX

Measurement of the specific refractive index involves the determination of relatively small differences. Furthermore the turbidity of these sols restricts the use of commercial refractometers to quite low concentrations.

In spite of these difficulties use of the Zeiss dipping refractometer was found feasible. Consideration of the average deviation of instrumental readings and the temperature coefficient of refractive index indicated that temperature control of $\pm$ 0.1° C. was adequate for successive determinations of refractive

indices of solvent and solution. By the use of the auxiliary prism, clear definition was obtainable up to a concentration of 15 gm. per litre.

The value of $\frac{d\mu}{dc}$ can be expected to be constant for all concentrations. This was verified by experiment (Fig. 5). The value of $\frac{d\mu}{dc}$ can thus be calculated from *one* measurement of the solvent and *one* of the polymer solution of suitable concentration. The resultant precision is 1 to 2%.

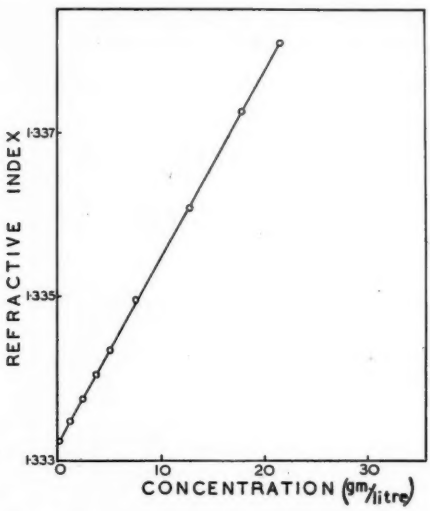

FIG. 5. *Refractive index of latex of different concentrations.*

It is worth noting that the value of $\frac{d\mu}{dc}$ may be *calculated* in certain cases, namely, when the refractive index of the suspended particle is known, and is independent of the composition of the medium. In this case $\frac{d\mu}{dc}$ is equal to the difference of refractive index of the suspended particle and of the medium divided by the density of the suspended phase. This is particularly useful when the sol to be investigated is very dilute.

Finally μ_0 is the refractive index of the liquid in which the particle is suspended. For example, in this work the medium is a 0.1% solution of soap.

(*c*) MEASUREMENT OF CONCENTRATION

The concentration in grams per cubic centimetre was calculated from a gravimetric determination of the material which is non-volatile at 60° C. in a vacuum oven.

Particle density was obtained by use of a pycnometer.

Agglomeration on Dilution

The high turbidity of latex to visible radiation made dilutions of 10 to 100 volumes necessary. When water was used, an appreciable agglomeration took place, resulting in slow increases in specific turbidity with time. This instability was overcome by using as diluent a 0.1% soap solution. Such dilution might be avoided completely, if necessary, by the use of infra-red radiation or of thinner absorption cells.

Application of Method to GR-S Latex

The technique described above was applied to the determination of the size of polymer particles present in a series of synthetic rubber latices. These latices represent different stages of conversion of monomers into rubber macromolecules.

In addition to the method of light scattering, an independent method was applied by Mr. J. Wright in this laboratory, based on the fact that the total surface of the dispersed phase of such an emulsion may be determined and hence an average particle size calculated.

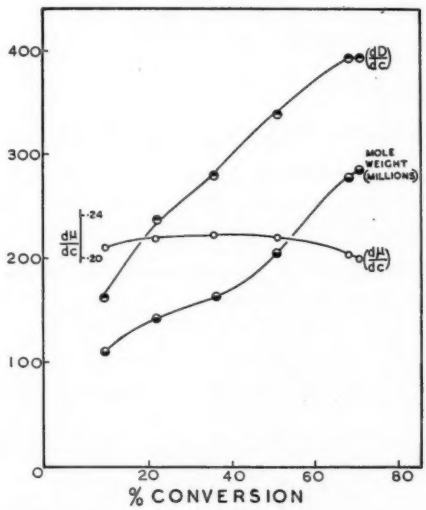

FIG. 6. *Changes of specific turbidity, specific refractive index, and particle size of latex during polymerization.*

Fig. 6 shows the values of specific refractive index, specific turbidity, and mole weight at different conversions as determined by means of the optical measurements. It is noted that the growth of size is almost entirely reflected by changes in the specific turbidity. The small variations of specific refractive index are due to changes in composition of the polymer particles.

In Fig. 7 is shown a comparison of mole weights determined by the light scattering and surface area methods.

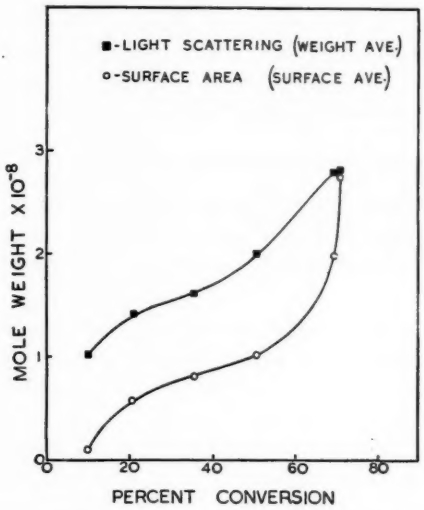

FIG. 7. *Comparison of particle size by light scattering and surface area methods.*

Discussion of Experimental Results

It is not the object of this paper to discuss the implications of these results in the synthesis of rubber, but rather to draw attention to a technique by which the size of particles of this nature may be evaluated.

In general, the results found for latex particles by this method agree with those found with the electron microscope.

The observed differences in size in Fig. 7 can be attributed to two factors. First, the light scattering method includes the total mass, whereas that of surface area does not include the emulsifier. Second, while light scattering gives a weight average particle weight, $\frac{\Sigma\, n_i\, m_i^2}{\Sigma\, n_i\, m_i}$, surface area gives a 'surface average',

$$\left[\frac{\Sigma\, n_i\, m_i}{\Sigma\, n_i\, m_i^{2/3}}\right]^3.$$

Only in the case of perfect homogeneity will these 'averages' coincide. Consequently the observed differences might be translated into a measure of the heterogeneity of particle size.

The slopes of the lines in Fig. 4 are due in part to the deviations from ideality expressed by the coefficient A_2 in Equation (2) and partly to secondary scattering.

Zimm (7) has recently evaluated the coefficient A_2. For rigid spherical particles

$$A_2 = \frac{4}{\rho M},$$

where ρ = particle density,

M = mole weight.

For non-spherical particles A_2 is greater, being a function of the ratio of length to diameter. This theory predicts a slope of -8 for the lines of Fig. 4. Considerable deviation from this value is found in the case of the largest particles. This suggests that some of these particles are not spherical.

Inasmuch as the phenomenon of secondary scattering (optical diffusion) is superimposed on the usual aberrations from ideal osmotic behaviour, these conclusions with respect to particle shape must be regarded as tentative.

Finally it should be pointed out that this method is rapid and highly reproducible. Moreover, although an expensive instrument has been used for the measurements discussed here, we have found that less expensive apparatus may be used. In general any instrument capable of light-scattering measurements or its equivalent, such as a turbidimeter or nephelometer, may be employed.

Acknowledgments

The authors wish to acknowledge the work of Mr. John Wright in the surface area measurements, and the assistance of Mr. Bruce Smith and of Mr. Randall Casson.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXI. CATALYTIC CRACKING OF CYCLIC ACETALS AND KETALS DERIVED FROM 2,3-BUTANEDIOL[1]

By A. C. Neish,[2] V. C. Haskell,[2] and F. J. Macdonald[2]

Abstract

Pyrolysis of the vapour of the cyclic methyl ethyl ketal of *l*-2,3-butanediol gives butanone as the chief product. Catalysts such as alumina or phosphoric anhydride greatly accelerate this reaction, while catalytic nickel has little effect. It was found necessary to have alkyl or aryl radicals substituted on the 1,3-dioxacyclopentane ring to obtain a rapid reaction. The molecule always splits symmetrically with respect to oxygen, and yields up to 90% conversion per single pass were obtained at moderate flow rates with rings substituted in the 2-, 4-, and 5-positions. The compounds tested were the formal, acetal, benzal, 2-ethylhexal, dimethyl ketal, and methyl ethyl ketal of *l*-2,3-butanediol and the *n*-butyral of ethanediol.

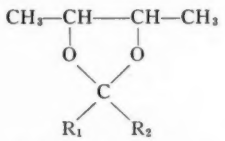
It has been shown in a previous paper (6) that 2,3-butanediol can be converted to its cyclic methyl ethyl ketal, in yields 95% of the theoretical value, merely by distilling it under reduced pressure in the presence of sulphuric acid. Because of the ease of preparation of this and other ketals and acetals (7, 9) from a fermentation product, it was thought that a study of their chemical properties would be of value.

It is known that cyclic acetals and ketals are resistant to alkaline hydrolysis but are readily hydrolysed by dilute acids; other than this there is little information in the literature on their chemical properties. The acetals of monohydric alcohols have been studied more fully. Claisen (2) found that they decomposed on heating, losing a mole of the alcohol, to give unsaturated ethers, e.g.,

$$CH_3 . CH(OC_2H_5)_2 \longrightarrow C_2H_5OH + CH_2 = CHOC_2H_5 .$$

He found that the reaction was catalyzed by quinoline and phosphoric anhydride. Sigmund and Uchann (8) prepared unsaturated ethers by passing acetal vapours through a heated tube packed with nickel or porous clays. This type of reaction has been patented by Herrmann and Deutsch (3).

This paper is chiefly concerned with the pyrolysis of cyclic acetals and ketals of the general formula:



levo-4,5-Dimethyl-2R_1-2R_2-1,3-dioxacyclopentane

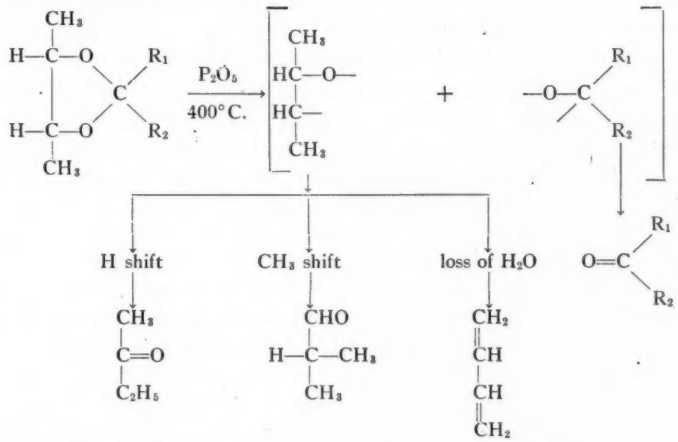
[1] *Manuscript received December 5, 1946.*

Contribution from the Division of Applied Biology, National Research Council Laboratories, Ottawa, Canada. Issued as Paper No. 49 on the Industrial Utilization of Wastes and Surpluses and as N.R.C. No. 1535.

[2] *Biochemist, Industrial Utilization Investigations.*

It has been found that the methyl ethyl ketal ($R_1 = CH_3$, $R_2 = C_2H_5$) is fairly resistant to pyrolysis in a Pyrex tube but its decomposition is greatly accelerated by alumina or phosphoric anhydride, although a catalytic nickel surface had little or no effect (see Table I). The chief product of the decomposition is butanone, particularly when phosphoric anhydride is used as the catalyst. The alumina catalyst causes formation of high boiling liquids, probably from the butanone.

The phosphoric anhydride catalyst was used for extending this work to related compounds (see Table II). The catalyst was reactivated between each experiment and in this way it was found possible to maintain its activity at an approximately constant level. In general all compounds give the same type of cleavage, i.e., the ring splits symmetrically with respect to oxygen to give butanone and the aldehyde or ketone originally used in preparing the compound. Isobutyraldehyde and easily condensed gases (butenes and butadiene) are obtained in small yields at the expense of the butanone (Table II). The general reaction may best be represented by decomposition to free radicals and rearrangement as follows:



A similar mechanism has been proposed by Bourns and Nicholls (1) to explain the formation of butanone and isobutyraldehyde during the direct dehydration of 2,3-butanediol.

It is interesting to note (Table II) that when R_1 and R_2 are light groups the cleavage takes place with difficulty and a relatively large amount of isobutyraldehyde is formed. This may mean that the shift of a H · or CH_3 · group occurs before the two fragments are completely separated and the shift of the methyl group occurs more readily when R_1 and R_2 are small for steric reasons. The slow decomposition of the formal or acetal might possibly be attributed to poisoning of the catalyst by the reactive aldehydes formed. That this is *not* so was demonstrated by passing an equimolecular mixture of the formal and

methyl ethyl ketal over the phosphoric anhydride catalyst at 400° C.; the former was 1.6% decomposed and the latter to the extent of 75.4%.

Hence it may be concluded that the rate of decomposition of these compounds is accelerated by having large substituents on the ring. Under conditions similar to those used for the experiments in Table II the *n*-butyral of ethanediol was 42% decomposed in a single pass to give butyraldehyde and acetaldehyde. This shows that substituents in positions 4 and 5 of the 1,3-dioxacyclopentane ring are not necessary for this type of cleavage to occur, although they may be helpful.

Experimental

Preparation of the 1,3-Dioxacyclopentane Derivatives

The cyclic acetals and ketals of *l*-2,3-butanediol were prepared as previously described (7). The *n*-butyral of ethanediol (2-propyl-1,3-dioxacyclopentane) was prepared similarly by treating an equimolecular mixture of ethanediol and butyraldehyde with a small amount of hydrochloric acid. It was obtained as a colourless liquid (b.p. 132° C.) in a yield 73% of the theoretical value. The boiling point agrees with the value previously given for this compound prepared by a different method (4).

Pyrolysis of the 1,3-Dioxacyclopentane Derivatives

The vapour was passed at a constant known rate through a Pyrex tube at atmospheric pressure. The tube was heated by an electric furnace, the temperature being controlled by a variable transformer within ± 2° C. The heated portion of the tube had a volume of 125 ml. A constant flow of vapour was obtained by passing the liquid into a preheater at a constant rate and completely vapourizing it. The rate of flow of the liquid was controlled by a needle valve and measured with a drop-counter. A one-litre Erlenmeyer flask containing about 400 ml. served as the liquid reservoir; it was mounted high enough so the pressure in the liquid line did not decrease more than 2% during an experiment. The amount of the ketal used in each experiment (about 300 gm.) was measured by weighing the reservoir to the nearest tenth of a gram at the beginning and end of each experiment, and the rate of flow calculated by dividing this value by the time.

The products of the pyrolysis passed into a water cooled reflux condenser. A cold trap immersed in dry ice – acetone slush was connected to the top of the condenser in order to obtain easily liquefied gases. The amount of gas passing through the cold trap, if any, was measured by collection over water. In this way it was possible to measure the number of moles of gas not condensed in the cold trap, as well as the weight of liquids and easily liquefied gases.

Examination of the Easily Liquefied Gases

In one experiment (No. 6, Table I) this fraction was purified by redistillation, at room temperature and atmospheric pressure, into another cold trap cooled in dry ice – acetone slush. The small residue from this distillation was added to the liquid products. The distillate was brominated in carbon

tetrachloride, starting at a temperature of −70° C. and finishing at room temperature. The solid product of the bromination was recrystallized and pure butadiene tetrabromide, m.p. 110° C., was obtained, which on mixing with an authentic sample showed no depression of the melting point. The yield corresponded to only 0.0031 mole of butadiene per mole of ketal decomposed. Distillation of the liquid bromides gave a constant boiling fraction, b.p. 83° C. (80 mm.), with a density of 1.776 and a refractive index of 1.510 at 28° C. These properties are similar to those of the 2,3-dibromobutanes. The yield was 0.008 mole per mole of ketal decomposed (25% of the liquid bromides). No other easily liquefied gases were identified. In subsequent experiments no attempt was made to analyse this fraction other than to check its boiling point, which was always in the butene–butadiene range.

Examination of the Liquid Products

The liquid products from the pyrolyses were separated by distillation through an efficient column filled with glass helices or Stedman packing. Butanone and isobutyraldehyde were identified by preparation of the 2,4-dinitrophenylhydrazones; the mixed melting points with authentic samples showed no depression. Other liquid products were identified by refractive index and boiling point. The small fractions between pure cuts were analysed approximately by determining their refractive indices. Fractionation of the higher boiling liquids (Table I) gave no pure fractions, partly because the products condense further on heating.

TABLE I

PYROLYSIS OF THE CYCLIC METHYL ETHYL KETAL OF *l*-2,3-BUTANEDIOL

Expt. No.	Catalyst	Temp., ° C.	Rate of ketal addition[1]	% Ketal decomposed	% Liquids obtained[2]	Products per mole of ketal decomposed			
						Moles of butanone[3]	Gm. of higher boiling liquids	Gm. of liquefied gases	Moles of gas
1	None	500	0.116	13.7	97.0	0.90	Nil	Nil	0.07
2	None	600	0.236	39.2	86.4	0.39	Nil	8.87	0.30
3	Ni on asbestos	400	0.530	15.5	93.5	0.91	Trace	Trace	0.29
4	Al_2O_3	300	1.021	75.0	98.7	1.49	17.0	Trace	Nil
5	Al_2O_3	380	1.138	89.4	95.7	1.39	24.4	2.3	Trace
6	Al_2O_3	450	0.568	88.5	90.9	1.25	39.8	4.8	0.20
7	P_2O_5 on pumice	400	0.328	53.2	99.0	1.99	Nil	Nil	Nil

[1] *Moles per 100 ml. of catalyst space per hr.*

[2] *Includes easily liquefied gases (caught in cold trap at −70° C. and atmospheric pressure).*

[3] *May contain a small amount of isobutyraldehyde.*

Preparation of Catalysts

The nickel catalyst was prepared by pyrolysis of asbestos soaked with nickel nitrate, followed by reduction with hydrogen. Phosphoric anhydride supported on pumice was prepared by King's method (5). It was reactivated

TABLE II

CATALYTIC CRACKING OF CYCLIC ACETALS AND KETALS OF *l*-2,3-BUTANEDIOL[1]

Reactant	Input rate[2]	Per cent decomposition	Per cent liquids obtained	Moles of products per mole of reactant decomposed[3]			
				Butanone	Isobutyraldehyde	Condensed gases[4]	Other carbonyl compounds[5]
Formal	0.463	2.7	99.8	—	—	—	—
Acetal	0.346	33.0	99.1	0.57	0.25	0.13	0.82
Dimethyl ketal	0.328	78.4	99.4	0.69	0.16	0.10	0.99
Methyl ethyl ketal	0.305	86.2	99.0	1.79	0.04	0.09	—
Benzal	0.408	80.3	98.4	0.85	0.05	0.10	0.91
2-Ethylhexal	0.297	89.0	96.5	0.65	0.08	0.15	0.90

[1] *The phosphorus pentoxide on pumice catalyst was used at 400° C. and atmospheric pressure; it was reactivated between each experiment.*

[2] *Moles per 100 ml. of catalyst space per hr.*

[3] *High boiling residues were obtained in 1 to 2% yields from each fractionation.*

[4] *Gases not condensed above −70° C. were obtained in negligible amounts. The condensed gases consist of butadiene and butenes.*

[5] *The carbonyl compound obtained is the one used in preparing the ketal; the acetal gives acetaldehyde, the dimethyl ketal gives acetone, the benzal gives benzaldehyde, and the 2-ethylhexal gives 2-ethyl hexaldehyde.*

by passing air through it at 400° C. for several hours, and then burning a piece of red phosphorus in the mouth of the tube. The batch used for the experiments reported in Table II was more active than that used for the single experiment reported in Table I. However, it was found that the activity of the catalyst (Table II) was kept fairly constant from one experiment to another by reactivation. This was checked by pyrolysing the same compound several times.

Activated alumina (Table I) was prepared by precipitating aluminium hydroxide from a solution of aluminium nitrate by ammonia. The filter cake, obtained by washing on a Büchner funnel, was dried at 150° C. and then broken up in a porcelain mortar. Particles 5 to 20 mesh were used.

Pyrolysis of Butanone in Presence of Alumina

Anhydrous butanone vapour was passed through a tube packed with the alumina catalyst (400° C.) at the rate of 1.09 moles per 100 ml. of catalyst space per hr. Twenty-three per cent was converted to other products. For each mole converted, 3.9 gm. of easily liquefied gases, 36.4 gm. of higher boiling liquids, and 0.017 mole of uncondensed gases were obtained. These products resemble those obtained from the methyl ethyl ketal of *l*-2,3-butanediol (Table I); it is quite possible that the ketal is cleaved quantitatively to butanone by the alumina catalyst and the other products are then formed from the butanone.

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THE REACTION OF CYANOGEN WITH 1,3-BUTADIENE[1]

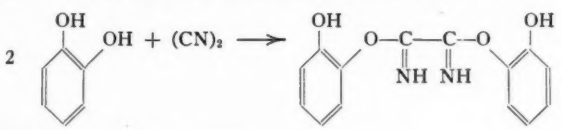
By G. J. Janz,[2] R. G. Ascah,[3] A. G. Keenan[4]

Abstract

Cyanogen and butadiene have been found to react. The main product of the reaction was identified as 2-cyanopyridine. Some 2,2′-dipyridyl and a number of unidentified compounds were also found present in the product in small yields. No evidence for the presence of β-hydromuconononitrile could be found. The reaction has been studied at atmospheric pressure in the vapour phase, and in ether solution, and at superatmospheric pressures in steel or glass bombs. In all cases the course of the reaction was essentially the same, 2-cyanopyridine being the main product. The formation of 2-cyanopyridine from butadiene and cyanogen is formulated as a Diels–Alder synthesis, in which the primary adduct undergoes a dehydrogenation to yield the final product. This is the first time to our knowledge that cyanogen has been reported as a dienophile in the diene synthesis.

Introduction

There are very few references in the literature to a reaction between cyanogen and an unsaturated hydrocarbon. The chemistry of cyanogen is such as to make this an interesting field for study. Cyanogen may be regarded as the dinitrile of oxalic acid since it is formed by dehydration of oxamide, and also on hydrolysis will give oxalic acid. In many respects cyanogen and its derivatives are closely related to the halogens and their derivatives; for example, on aqueous alkaline hydrolysis of cyanogen, a cyanide and cyanate are formed just as a chloride and hypochlorite are formed by a similar hydrolysis of chlorine. Thus it seems that cyanogen may react either by virtue of its (CN) groups, or by a dissociation of the molecule. The published literature on the reaction of cyanogen with various organic compounds gives further evidence of this dual behaviour. Merz and Weith (15) reported that on reaction of cyanogen with benzene at moderately high temperatures they obtained benzonitrile. Machek (13, 14) in a study of the reaction of cyanogen with phenols claimed there was nuclear substitution, and reported that 3-cyanocatechol had been obtained from catechol and cyanogen. This was later disproved by Hahn and Leopold (9) who showed that the reaction with phenols in all cases was such that the phenolic hydroxyl group combined with the triple bond of the (—C≡N) group, and never with the (C—C) bond of the cyanogen. The reaction with catechol was shown to be



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The reaction of cyanogen with diazomethane reported by Azzarello (2) to give cyanosotriazol is of interest since in this case the (—C≡N) group of the cyanogen is found as part of the ring structure in the final product. Tollens and his associates (18, 19) reported an attempt to add cyanogen to a double bond. By prolonged bubbling of cyanogen through allyl alcohol, an oil was obtained the analysis of which corresponded to $C_3H_5(CN)_2OH$. Among the products obtained on its hydrolysis they reported oxamide, and it would seem that the (C—C) bond of the cyanogen was not broken in the formation of this compound.

It seemed reasonable therefore to expect either a straight chain addition product, a cyclic addition product, or both from a reaction of cyanogen and butadiene. The primary object of our investigation was to attempt the reaction of cyanogen with butadiene. When it was found that a reaction occurred, the work was extended to determine the effect of reaction variables on the course of the reaction.

Experimental

Materials

For the laboratory preparation of cyanogen a modification of Hahn and Leopold's apparatus (9) was used for the reaction between sodium cyanide and copper sulphate. The hydrogen cyanide in the gas was absorbed in aqueous silver nitrate and the moisture was removed by phosphorus pentoxide towers. The dry cyanogen was finally condensed at −80° C. It was stored in a steel pressure cylinder at room temperature. It has been found that if the cyanogen is pure and dry it may be maintained safely thus for several months.

The butadiene was that obtained from the Matheson Company and was used without further purification.

Apparatus

The reaction was studied at atmospheric pressure in the vapour phase, and in ether solution, and at superatmospheric pressures in steel and glass vessels.

For the vapour phase study the size of the reactor varied from a small all-glass system used for the scouting work to a large steel reactor used for the more detailed study of the reaction conditions. The arrangement of the reactor and the rest of the apparatus is shown in Fig. 1. For the temperature–time series of experiments the reactor was made from a 2 in. steel pipe, 21 in. long, with a thermocouple well of $\frac{1}{4}$-in. pipe extending down the centre of the large pipe, and a removable flange head on the bottom. The volume of the reaction chamber *E* was 920 ml. It was covered with two layers of asbestos sheet, and then wound in three sections with nichrome resistance spirals, each being 30 ohms (0.665 Ω/ft.), and finally thermally insulated with a heavy piece of asbestos steam pipe lagging. This steel reactor was used for all runs of 10 to 150 sec. contact times. For exceedingly short contact times, one second or less, a silica reactor was used. It was made from a silica tube

20 in. long, and 0.25 in. inside diameter, and was also electrically heated. Temperature measurements were made with a chromel–alumel thermocouple and an L. & N. potentiometer indicator. Table I gives representative values of the temperature gradient in the reactor during three different trials; the measurements start from the bottom of the thermocouple well.

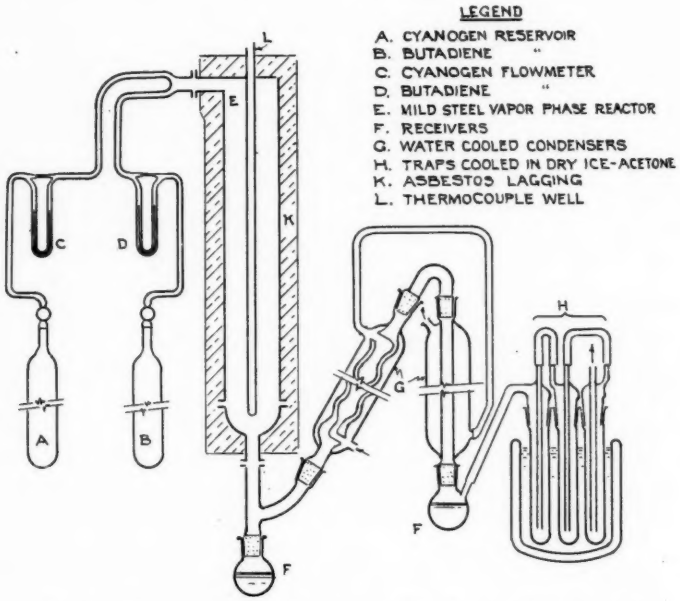


FIG. 1. *The arrangement of the apparatus for the vapour phase study.*

TABLE I

TEMPERATURE GRADIENT OF 2 IN. MILD STEEL REACTOR

Position of thermocouple, in.		0	2	4	6	8	10	12	14	16	18	20
Temperature, °C.	(1)	539	607	650	664	666	666	664	664	661	642	593
	(2)	481	542	579	586	586	586	586	586	584	570	528
	(3)	379	440	471	478	480	480	485	490	485	471	443

The gas reservoirs were small steel laboratory gas cylinders fitted with sensitive needle valves. The flowmeters were of the standard constriction type, and each was calibrated with the gas being used with it. A saturated aqueous solution of sodium chloride containing 10 cc. concentrated hydrochloric acid per litre (17) was used as the indicator liquid for the cyanogen flowmeter, and corn oil for the butadiene flowmeter. For cooling the gases and stripping

out the reaction product, two water cooled condensers were used. Finally the unreacted butadiene and cyanogen and more volatile products were condensed at −80° C.

A few experiments were made with butadiene and cyanogen under superatmospheric pressures to observe the course of the reaction under these conditions. The apparatus used consisted of glass bomb tubes, a stainless steel bomb, and the standard high pressure AMINCO hydrogenation equipment.

Procedure and Results

1. *The Reaction of Cyanogen with Butadiene*

(i) *The Reaction*

Cyanogen and 1,3-butadiene in a molar ratio of 1.0 : 1.0 were passed through the vapour phase reactor for a total time of 13 hr. The temperature of the reactor was maintained at about 480° C., and the contact time of the gases in the reaction zone was about 98 sec. The total recovery, as liquid product and unreacted butadiene and cyanogen, was about 84.5% by weight of the initial material input. The yield of product, stripped from the gases leaving the hot reaction zone by the water-cooled condensing system, was about 38.5% by weight, calculated on the total input of butadiene and cyanogen. After removing the more volatile portions, fractional distillation at 8 to 12 mm. of mercury pressure in a Whitmore–Fenske column was used to investigate the crude liquid product. It was separated into three fractions; (*a*) a low boiling fraction, (*b*) an intermediate boiling fraction, about 47% by weight of the crude product, and (*c*) a high boiling fraction.

(ii) *The Reaction Products*

The intermediate boiling fraction (*b*) above was identified as 2-cyanopyridine. It was separated from the crude product by fractional distillation, as mentioned above, and further purified by filtering off the crystals at 0° C., and then washing and recrystallizing several times from cold ether. The physical properties found for our product and for those quoted in the literature for 2-cyanopyridine are: m.p. obs. 27.0° to 27.5° C., lit. 29° C., 26° C., (4); b.p. found 222° to 227° C., lit. 212° to 215° C. (4), 222.5° to 223.5° C. (7). Found: C, 70.00; H, 4.07; N, 26.04%. Calc. for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.91%. In order to identify this product, picolinic acid hydrochloride was prepared by subjecting the 2-cyanopyridine to hydrolysis with aqueous sodium hydroxide and separating the acid as the hydrochloride. The results of the analysis for the picolinic acid hydrochloride were as follows: Found: C, 45.44; H, 4.21; N, 8.55; Cl (ionic), 21.83; (total), 21.95%. Calc. for $C_6H_6NO_2Cl$: C, 45.15; H, 3.79; N, 8.78; Cl, 22.23%. From the picolinic acid hydrochloride prepared in this manner, the free picolinic acid was prepared by mixing with a half molar equivalent of barium hydroxide and extracting the free acid with chloroform. The picolinic acid thus isolated, after recrystallization from dioxane, and sublimation, was found to have a melting point of 135° to 136° C. (lit. 136° to 137° C. (10), 134.5° to 136° C. (4)). By heating

the 2-cyanopyridine with lime, pyridine was separated from the mixture by distillation (b.p. found 114.7° C.; lit. 115.3° C.; N_D^{26} found 1.505, lit. 1.507). The pyridine was further identified by comparing the X-ray diffraction pattern of its picrate with that from an authentic sample of pyridine.

A particular effort was made to detect the presence of β-hydromuconononitrile (b.p. 110° C. (2 mm.); m.p. 74° to 75° C. (6)) in the low and high boiling fractions of the reaction product. The low boiling fraction included all the distillate taken off before the 2-cyanopyridine fraction, the upper limit in distillation range generally being about 70° C. at 2 to 3 mm. pressure. From the vapour phase runs at the lower temperatures (up to 500° C.) the low boiling fraction was found to be mainly 4-vinylcyclohexene. Careful fractionation of a low boiling fraction from a run at 600° C. indicated that it was composed of several liquids boiling in the range of 55° to 210° C. (760 mm.), and with very little 4-vinylcyclohexene present. The more complex nature of this fraction at the higher temperatures is to be expected since 4-vinylcyclohexene is unstable at temperatures above 500° C. (3), and since aromatic compounds are formed from butadiene at high temperatures (11). Investigation of the fraction of the crude product boiling higher than 2-cyanopyridine established the presence of 2,2′-dipyridyl. It was separated in the Whitmore–Fenske column at 133° to 134.5° C. (11 mm.), and was found to have the following properties: m.p. (impure) 56.6° C.; b.p. 270° to 272° C. (760 mm.); picrate, m.p. 154° to 155.5° C.; gave characteristic rose red colour reaction with ferrous ions (lit. for 2,2′-dipyridyl, m.p. 69.5° C., b.p. 272.5° C. (760 mm.); picrate m.p. 154° to 155.5° C.; gives characteristic rose red colour reaction with ferrous ions). Two other products *A* and *B* were also isolated from the high boiling fractions of the high temperature runs (700° C.), but were not further investigated when it was found that they were not β-hydromuconononitrile. Unknown *A*, (b.p. 77° to 80° C. (3 mm.), m.p. 71° to 72° C., N analysis 23.4%) was not β-hydromuconononitrile (m.p. 74° to 75° C., N calc. 26.4%) because the mixed melting point was considerably depressed, and the X-ray diffraction patterns of the two were quite different. The unknown probably is 2-cyano-2-picoline (m.p. 87.5° to 88° C., N calc. 23.7%) since the mixed melting point of these two was around 76° to 81° C., and the X-ray diffraction pattern of these two was identical. Unknown *B* was found to have a melting point of 185° to 190° C., and obviously was not β-hydromuconononitrile.

2. *The Temperature–Contact Time Study of the Vapour Phase Reaction*

The temperature range of 400° to 700° C. and the contact time range of 0.5 to 120 sec. were investigated. A standard procedure was used for this series of experiments. The reactants were introduced in approximately equimolar proportions. During the run the rate of input of gases was followed by the flowmeter readings, and the temperature of the reactor at the 12 in. mark was observed every 15 min. The total temperature gradient was generally checked twice during a trial. The analysis of the crude product was

carried out by a distillation at reduced pressure in a Whitmore–Fenske column. The data of these runs are given in Table II.

TABLE II

DATA ON THE REACTION OF BUTADIENE AND CYANOGEN IN THE VAPOUR PHASE

Temp., °C., (approx.)	Duration of runs, hr.	Contact time, sec.	Reactant ratio butadiene: cyanogen, moles	Total material recovery, % of input by weight	Crude liquid product, % of input by weight	2-Cyano-pyridine, % of crude product by weight	2-Cyano-pyridine, % of input by weight
470–490	1.66	23	1.28 : 1.0	85.5	18.7	33	6.17
470	2.5	69	0.93 : 1.0	67	30.5	39	11.9
480	13.0	98	1.0 : 1.0	84.5	38.5	47	18.1
700	3.0	0.39	1.0 : 1.0	77.6	13–14	41.5	5.6
700	12.5	0.88	1.15 : 1.0	55	29.7	27	—
700	1.5	18	1.18 : 1.0	45	27	23	6.3
700	17.5	32.5	0.97 : 1.0	54	43.9	24	10.5
700	9.6	33	0.89 : 1.0	58	43	24	10.3
680	8.0	37	0.77 : 1.0	53.7	36.6	33	12.1
700	2.75	90	0.82 : 1.0	39	34	16	5.5

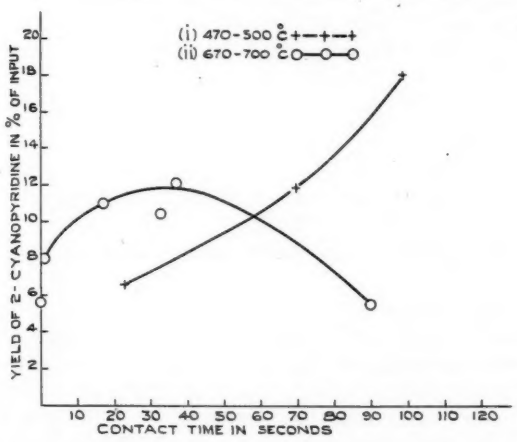


FIG. 2. *The relation between yield of 2-cyanopyridine and contact time.*

The relation between the yield of 2-cyanopyridine and the contact time is most clearly seen by considering the results graphically in Fig. 2.

In the temperature range of 470° to 500° C., it seems that the yield of 2-cyanopyridine increases with increasing contact time. The best yield, 18.1% of 2-cyanopyridine per gram input reactants, is obtained using a contact time of 98 sec. From the curve it seems that this yield would probably increase with an increase in contact time. Pyrolysis of the products and reactants could also be expected to increase with increasing contact time, and this

effect may become great enough to swamp any increase in yield of 2-cyanopyridine. This trend was indicated when contact times over 200 sec. were employed.

The effect just mentioned is clearly evident from the results in the temperature range of 670° to 700° C. This curve shows that the yield of 2-cyanopyridine increases with increasing contact time to a maximum of about 12.1% when the contact time has reached 36 sec. At longer contact times the yield drops, probably because the pyrolysis effect is masking any increase of yield in 2-cyanopyridine.

The results of the yield–temperature study are also presented graphically in Fig. 3 to show the relation between the yield of 2-cyanopyridine and the temperature of the reaction zone more clearly.

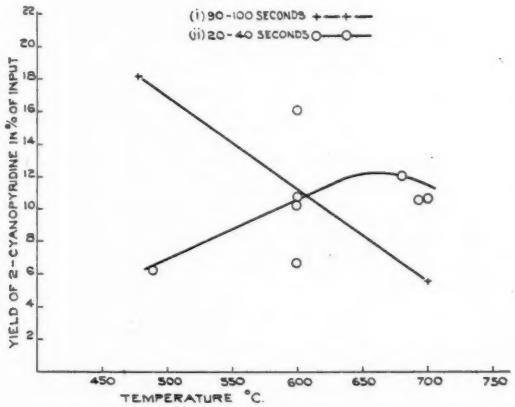


FIG. 3. *The relation between yield of 2-cyanopyridine and temperature of reaction zone.*

Using a relatively long contact time (90 to 100 sec.) the yield of 2-cyanopyridine is greatest (18.1%) at about 480° C., and decreases with increasing temperature to a value of about 5% at 700° C. This curve probably shows the effect of pyrolysis at high temperatures more clearly than the previous graph. At shorter contact times (20 to 40 sec.) the yield of 2-cyanopyridine increases with increasing temperatures from about 6% at 480° C. to about 12.1% at 680° C. The lower yields at 700° C. probably indicate that the pyrolysis effect is becoming great enough to mask any increase in yield of 2-cyanopyridine.

In the region investigated, the optimum conditions would seem to be a temperature of about 480° C., and a contact time of about 90 to 100 sec.

3. *The Vapour Phase Reaction in the Presence of Hydrogen*

Since the formation of 2-cyanopyridine from butadiene and cyanogen is postulated as involving a dehydrogenation, the vapour phase reaction was carried out in the presence of hydrogen to see if the course of the reaction

would be altered. The apparatus and set-up for this study was modified only to permit the introduction of hydrogen gas along with the mixture of reactants. A series of runs was made with the ratio of butadiene to cyanogen being about equimolar while the hydrogen to butadiene or cyanogen ratio was varied from five to one, to approximately equimolar. The reaction product was investigated in the usual manner. In Table III the operational data and experimental results for these experiments are listed.

TABLE III

DATA ON THE REACTION OF BUTADIENE AND CYANOGEN IN PRESENCE OF HYDROGEN

Trial	Temp., °C. (approx.)	Contact time, sec.	Molar ratio of gases			Material recovery	Crude yield
			H_2 :	Butadiene :	Cyanogen	% by weight calc. on input of butadiene and cyanogen	
(1)	470	22	5.03	1.05	1.0	82	0
(2)	470	24	1.4	1.1	1.0	84	7
(3)	470–490	23	0	1.28	1.0	85.5	18.7

No reaction was observed with a large excess of hydrogen present. With a more nearly equimolar ratio of gases a slight reaction was observed. Two similar trials were made at 700° C., and here, with approximately an equimolar ratio of the gases, the crude product was obtained in 33% yield, while with a threefold excess of hydrogen, only a 12% yield was obtained.

Examination of the crude product by distillation indicated that it was essentially the same as that obtained from the reaction in the absence of hydrogen, i.e., contains about 20% 2-cyanopyridine. The high boiling fraction however had a reddish colour instead of the usual yellow-green, and distillation yielded a series of fractions boiling over ranges of 10° C. or greater, which were not further investigated.

For purposes of comparison, the results of an experiment without hydrogen are listed in Table III. To see if the decrease in yield was due mainly to a dilution effect of the butadiene and cyanogen by hydrogen, two more experiments were made. The conditions for these runs were identical to those used in Runs 1 and 2, but instead of hydrogen, nitrogen (an inert gas) was used. There was no product formed when the nitrogen was used in fivefold excess to the others, and only a 10% yield of crude product when the nitrogen was decreased as in Run 2. The decrease in yield observed above is apparently due to a dilution effect of the butadiene and cyanogen by the third gas.

4. *The Vapour Phase Reaction in the Presence of Catalysts*

The question of a catalyst for this reaction has not been investigated to any great extent. The only catalysts tried were silica gel and 'Florex'. For these experiments a small all-glass reactor, similar in design to the large steel reactor, was used, with the rest of the experimental set-up about the same. The reaction in the presence of 'Florex' was carried out at 470° to 485° C. The

product was a moist brown solid from which a small amount of red oil could be extracted. When silica gel was used, the reactor was operated in the range 100° to 300° C. and at 400° C. In both cases the catalyst became quite black and at 400° C. a moist brown solid product was also obtained. Two brands of silica gel, 'Davco' and 'Hyposil', were used. The brown solid was found to be quite soluble in concentrated sulphuric acid, and probably was paracyanogen (4).

From the above results it seems that silica gel and 'Florex' promote only a simultaneous decomposition and polymerization of cyanogen, and do not catalyze the formation of 2-cyanopyridine.

5. *The Reaction under Superatmospheric Pressures*

Several trials were carried out in glass bomb tubes at about 100° C. Butadiene and cyanogen, about 5 to 7 gm. each, were sealed in glass and heated for periods varying from 21 to 33 hr. in a furnace at 100° ± 10° C. From these there was recovered unreacted butadiene and cyanogen and an oil (21 to 31% yields). This oil contained about 55% by weight of 2-cyanopyridine, the remainder being mainly 4-vinylcyclohexene. When the trial was carried out in a steel bomb, fitted with a pressure gauge, a similar product was obtained at 105° C. The pressure developed in the vessel was 440 lb. per sq. in. One trial was made at 250° C., a temperature above the critical temperatures of both reactants. The high pressure AMINCO equipment was used for this work. The bomb was charged with 52 gm. of cyanogen, and 51 gm. of butadiene, and heated for a period of six hours to a maximum temperature of 270° C. The pressure rose to a maximum of 620 lb. per sq. in., and settled to a final value of 200 lb. per sq. in. The product was a black solid mass (62 gm.) from which a brown oil could be extracted (31 gm.).

Analysis of the oil by distillation showed it to be mainly vinylcyclohexene, and 2-cyanopyridine (26%).

The work in the bomb tubes indicates that the reaction of butadiene and cyanogen is essentially the same under superatmospheric pressures as at atmospheric pressures. The black solid product observed in these experiments was not investigated, but probably contains a considerable amount of paracyanogen (5).

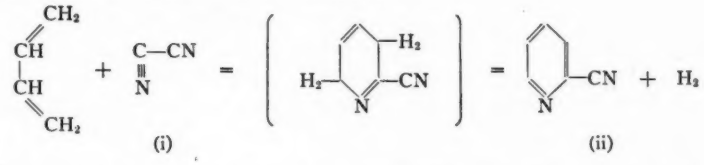
6. *The Reaction in Ether Solution*

There are some references (9, 18) to the reaction of cyanogen with organic compounds in an inert solvent. It was of interest therefore to attempt the reaction of cyanogen and butadiene in ether solution at room temperature. Slow streams of butadiene and cyanogen were bubbled, under slight pressure, through about four litres of vigorously stirred ether. After some 47 hr. the experiment was stopped and the reaction mixture distilled. The high boiling residue remaining after all the solvent had been removed contained no combined nitrogen.

Butadiene and cyanogen apparently do not react in ether solution at room temperature.

Discussion

To account for the formation of 2-cyanopyridine, the reaction between cyanogen and butadiene may be formulated as:



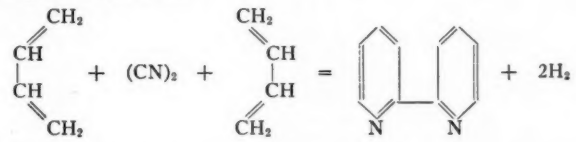
(i) (ii)

The first step of this involves a diene synthesis, well known as the Diels–Alder reaction, and the second a dehydrogenation of the adduct to give the final product. This is the first time to our knowledge that cyanogen has been reported as capable of acting as a dienophile in Diels–Alder reactions.

To date, the dienophiles in the generalized diene synthesis have been grouped into the following types, C=C—R and C≡C—R, in which R may be of the type that terminates in the carbonyl, acetonyl, nitro, sulphonyl, cyano, amino, or vinyl group, or even hydrogen, attached directly to one of the olefinic or acetylenic groups (16). An earlier investigation has shown that cyanobenzene can act as a dienophile although the authors did not point this out (8). The reaction involved was the preparation of pentaphenylpyridine from tetracyclone and cyanobenzene. The phenyl group served as R, and (C≡N) was the dienophilic component. By the work presented in the present report it has been shown that when R is the cyano group, the dienophylic component may be the (C≡N) group.

In this reaction, the intermediate adduct probably first formed is unstable under the conditions of the reaction, and by losing hydrogen forms 2-cyanopyridine. It is not unusual in a diene synthesis that, for a slowly reacting system, elevated temperatures and pressures must be used. The application of high temperatures to accelerate the reaction has its limits, however, because the diene synthesis is a reversible reaction, and in the case of exothermic reactions, equilibria are set up which are displaced more and more to the side of the reactants with increasing temperatures. As indicated above, however, the diene adduct spontaneously changes to a dehydrogenated product, and it may be this step that makes this synthesis possible at the high temperatures used.

The presence of 2,2′-dipyridyl in the reaction of cyanogen and butadiene may be explained by a possible reaction of two moles of butadiene with one of cyanogen, as follows:



by a mole of butadiene with 2-cyanopyridine.

From the experimental work it would seem that at temperatures less than 400° C. at atmospheric pressure the rate of reaction rapidly becomes so slow that no reaction is observed. At higher temperatures no straight chain addition product but rather 2-cyanopyridine was found. The catalyst search for this reaction was not pressed when it was suspected that a Diels–Alder synthesis was involved, since such a reaction is not sensitive to catalytic effects (1). It may be, since the reaction as postulated also involves a dehydrogenation, that the use of a suitable dehydrogenation catalyst in the optimum temperature range might affect the rate of the over-all reaction.

The results of this research have been covered in a recent patent (12).

Acknowledgment

The authors are indebted to J. H. Michell for the identification of 2-cyanopyridine and 2,2′-dipyridyl in the product.

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THE PREPARATION OF 2-CYANOPYRIDINES FROM CYANOGEN AND SOME SIMPLE 1,3-DIENES[1]

By G. J. Janz[2] and A. G. Keenan[3]

Abstract

In a previous paper, it was shown that cyanogen could be reacted with butadiene to give 2-cyanopyridine as the main reaction product. It was postulated that the reaction occurred through a Diels–Alder type of mechanism, with spontaneous dehydrogenation of the primary adduct. The present investigation has extended this study to the reaction of cyanogen with (i) isoprene, (ii) chloroprene, (iii) 2-methylpentadiene, and (iv) hexachlorobutadiene. The results are consistent with the mechanism postulated in the earlier paper.

Introduction

On studying the reaction between cyanogen and butadiene, it was found (7) that the main product of the reaction was 2-cyanopyridine. The formation of this product was explained as being due to a Diels–Alder reaction between cyanogen and butadiene, in which the primary adduct underwent a dehydrogenation to yield the final product. The role of cyanogen as a dienophile was novel. The primary object of the present research was to see if this behaviour of cyanogen could be generalized for other simple 1,3-dienes, namely, (i) isoprene, (ii) chloroprene, (iii) 2-methylpentadiene, and (iv) hexachlorobutadiene.

Experimental

Materials

Isoprene.—This was prepared from dipentene in 20% yields by pyrolysis. A nichrome wire spiral maintained at a dull red heat was suspended in the vapours of dipentene refluxing under a vacuum of 2 to 3 cm. of mercury (3, 6). The gases given off were passed through water cooled scrubbing towers and condensed in dry ice – acetone traps. The product from the pyrolysis was distilled in a Whitmore – Fenske column at atmospheric pressure. The fraction boiling from 34° to 38° C. was collected as isoprene (b.p. 34° C.). At least 95% of this fraction boiled in the range 34.5° to 35.5° C. The isoprene was prepared a few days before use and stored in a small steel cylinder provided with a needle valve.

Chloroprene (*2-Chlorobutadiene-1,3*).—This was received from E. I. du Pont de Nemours and Company in the form of a 50% solution in xylene containing a small amount of catechol as a stabilizer. It was distilled in a nitrogen atmosphere under a vacuum of 12 to 15 cm. through an 11 in. glass column

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packed with Berl saddles. The distillate was partly condensed in a water cooled receiver and more completely in a series of dry ice – acetone traps. Under atmospheric pressure the product boiled at 60° C. (lit. 59.4° C.).

2-Methylpentadiene-1,3.—This was obtained from E. I. du Pont de Nemours and Company and used without further purification.

Hexachlorobutadiene.—This was obtained as a sample from the Hooker Electrochemical Company. It was a colourless liquid, b.p. 210° to 220° C., f.p. −20° to −25° C., and formula $CCl_2=CCl-CCl=CCl_2$.

Cyanogen.—This was prepared from sodium cyanide and copper sulphate, as described previously (7).

Apparatus

The reactor used for the reaction of cyanogen with isoprene, chloroprene, and 2-methylpentadiene, was the mild steel reactor used for the vapour phase study of the reaction of cyanogen with butadiene (7). The experimental set-up was exactly as described (7) except that the method of feeding the dienes had to be somewhat modified. For the work with isoprene, a steam jacketed flowmeter was used, and the isoprene cylinder was immersed in a water bath maintained at 65° C. When chloroprene was used, it was fed as a liquid from a calibrated dropping funnel into a vaporizer maintained at 100° C. From this vaporizer the reactants (cyanogen and chloroprene) were led into the reactor. The same system was used for 2-methylpentadiene.

The reaction between hexachlorobutadiene and cyanogen was not tried in the vapour phase at atmospheric pressure, but only in glass bomb tubes at superatmospheric pressures.

Procedure

(*i*) *Cyanogen and Isoprene*

(*a*) *The Reaction*

With the reactor maintained at 490° C. at the 12 in. mark, isoprene and cyanogen were passed through for 155 min. at the rates of 21.4 and 15.4 gm. per hr., respectively (molar ratio 1 : 1). The contact time at these rates was about 90 sec. The crude product (a black pasty mass that set to a solid at 0° C.) was produced at the rate of 13.5 gm. per hr. This represents a material loss in the reaction of 38%. This crude product was shown by the reactions described below to contain at least 29.3% of cyanopicolines. Hence the latter were produced in at least 18% yield calculated on the total input of reactants.

(*b*) *The Identification of the Product*

The black crude product was distilled under vacuum in a Vigreux flask. This gave, among other fractions, one that boiled at 88.5° C. (2 mm.) and was a solid under ordinary conditions. Three crystallizations from ligroin gave a product melting at 48° to 77° C. This impure material gave the following analysis. Found: C, 71.18; H, 4.7; N, 23.4%. Calc. for $C_7H_6N_2$: C, 71.15; H, 5.12; N, 23.7%. This corresponds quite well to a

cyanopicoline. This material was hydrolysed by refluxing with aqueous sodium hydroxide and then decarboxylated by dry distillation with lime. The resulting liquid yielded on distillation a fraction boiling from 143° to 148° C. at atmospheric pressure. Mixtures of 3- and 4-picoline boil in the range 142° to 146° C. The above fraction was treated according to the procedure for separating 3- and 4-picolines through their zinc chloride salts (1, 5). The zinc chloride salt, after two recrystallizations from ethanol, was decomposed with potassium hydroxide to yield a colourless oil. The latter formed a yellow crystalline picrate which, after two crystallizations from ethanol, had a melting point of 161° to 162° C. The analysis was found to check well for picoline picrate. Found: C, 44.34; H, 2.77; N, 17.1%. Calc. for $C_{12}H_{10}N_4O_7$: C, 44.73; H, 3.13; N, 17.4%. According to the literature the melting point of 4-picoline picrate is 163° to 164° C., 167° C. (2), and 158° to 161° C. (1). A sample of authentic 4-picoline (Eastman Kodak Company) gave a picrate of melting point 163.5° to 164.5° C. The X-ray diffraction pattern of this picrate was identical with the one prepared from the unknown picoline.

From another decarboxylation of the crude product (m.p. 48° to 77° C.), the oil (b.p. 142° to 145° C.) was isolated and treated according to the procedure for the separation of the 3- and 4-picolines through their oxalates (9, 10). Three crystallizations gave an oxalate (m.p. 137.5° to 139° C.) that corresponded to the 4-picoline oxalate (lit. m.p. 139° to 140° C. (9), 137° to 138° C. (10)). Repeated crystallizations of both the oxalate and picrate formed from this fraction gave further products which were identified as 4-picoline derivatives. No evidence could be found for the presence of the 3-picoline derivative.

The original crude product (m.p. 48° to 77° C.) was further recrystallized repeatedly from ligroin. This yielded a white solid with a sharp m.p. of 87° to 88° C. and which gave an analysis that checked well for a cyanopicoline. Found: C, 71.80; H, 5.16; N, 23.6%. Calc. for $C_7H_6N_2$: C, 71.15; H, 5.12; N, 23.7%. This pure substance comprised well over 50% of the initial solid.

From this evidence we conclude that one product of the reaction between cyanogen and isoprene is 2-cyano-4-picoline. The presence of an isomeric cyanopicoline in the impure recrystallized product (m.p. 48° to 77° C.) is indicated by the over-all analysis. No attempt was made to elucidate its structure.

(*ii*) *Cyanogen and Chloroprene*

(*a*) *The Reaction*

The chloroprene and cyanogen were fed into the reactor at 20 gm. per hr. and 12 gm. per hr. respectively (molar ratio 1 : 1). The temperature was 500° C. and the contact time of the gases in the reaction zone was about 110 sec. The crude product was produced at the rate of about 9 gm. per hr. The total recovery as crude product and unchanged reactants was about 63%.

(*b*) *The Identification of the Product*

A fraction boiling at 140° C. (30 mm.) was separated from the product by distillation in a Vigreux flask. This fraction (about 15% by weight of the crude) crystallized to a green solid at room temperature. After several crystallizations from ether and ethanol, a white solid was obtained of melting point 107.5° to 108° C. Found: C, 51.86; H, 2.40; N, 20.55; Cl, 25.73%. Calc. for $C_6H_3N_2Cl$: C, 52.01; H, 2.18; N, 20.22; Cl, 25.59%. Hence this checks well for a chlorocyanopyridine.

From the reactor a black tarry mass was also recovered. It was extracted with ether, and the solid thus recovered was recrystallized twice from ethanol. This yielded a white crystalline material of melting point 83° to 84° C. Found: C, 51.92; H, 2.42; N, 20.1; Cl, 26.0%. Calc. for $C_6H_3N_2Cl$: C, 52.01; H, 2.18; N, 20.22; Cl, 25.59%. This also checks for a chlorocyanopyridine. This solid was hydrolysed with alcoholic (75% ethanol) sodium hydroxide solution. The reaction mixture was acidified with hydrochloric acid, evaporated to dryness, and the residue crystallized from water. A brown solid was obtained which darkened at 170° C. and melted with decomposition at 172° C. (lit. for 5-chloropicolinic acid, m.p. 169° to 170° C. (4) and 168° C. (2)).

One product of the reaction of cyanogen with chloroprene has thus been shown to be 5-chloro-2-cyanopyridine (m.p. 83° to 84° C.). An isomeric chlorocyanopyridine (m.p. 107.5° to 108° C.) also appears to be formed but its structure was not investigated further.

(*iii*) *Cyanogen and 2-Methylpentadiene*

(*a*) *The Reaction*

The cyanogen and 2-methylpentadiene were fed in at the rates of 13.2 gm. per hr. and 17.9 gm. per hr., respectively (molar ratio approximately 1 : 1). The reaction temperature was about 500° C., and the contact time about 121 sec. The total recovery, as crude product and unreacted materials, was 75% of the input and the crude product alone was about 61% of the input.

(*b*) *The Identification of the Product*

The crude product was filtered free of unreacted 2-methylpentadiene, and the resulting solid was recrystallized repeatedly from ligroin. A white crystalline material was thus obtained, with a melting point of 53° to 53.5° C. Found: C, 73.0; H, 6.1; N, 20.8%. Calc. for $C_8H_8N_2$: C, 72.7; H, 6.1; N, 21.2%. This corresponds well to a cyanolutidine. The yield was approximately 30%, calculated on the input. This material was hydrolysed in the usual manner with aqueous sodium hydroxide and then decarboxylated by dry distillation with lime. From this a liquid, boiling from 156° to 157° C. at atmospheric pressure, was isolated (lit. for 2,4-lutidine, b.p. 157° C., 159° to 159.5° C. (2)). From this oil a picrate was formed which, after recrystallization from ethanol, had a melting point of 179° to 180° C. (lit. for picrate of 2,4-lutidine, 179° C. (2)). This checks well for the 2,4-lutidine derivative.

It appears therefore that 6-cyano-2,4-lutidine is a product of the reaction of cyanogen with 2-methylpentadiene. No evidence for the formation of isomers was obtained in this case.

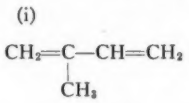
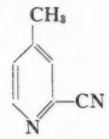
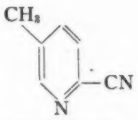
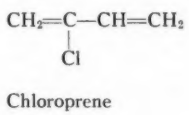
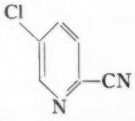
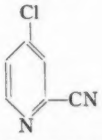
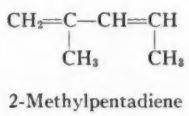
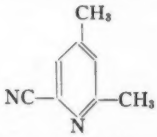
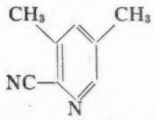
(iv). Cyanogen and Hexachlorobutadiene

In an attempt to react cyanogen and hexachlorobutadiene, approximately equimolar quantities of the two were sealed in glass bombs and heated in a furnace for 46 hr. at 150° to 170° C. About 86% of the hexachlorobutadiene was recovered unreacted. A small amount of black solid, similar to that observed in the high pressure work with cyanogen and butadiene (7), was also formed. No other solid reaction products were found. The experiment was repeated using reaction conditions of 37 hr. at 210° C. and 66 hr. at 230° C. In each case nearly all the hexachlorobutadiene was recovered unreacted and no evidence of addition products was found.

Discussion

Under the conditions investigated, cyanogen reacts with isoprene, chloroprene, and 2-methylpentadiene, apparently through the triple bond of the CN group, forming substituted pyridines. On the assumption that no nuclear migration of the CN group takes place during the reaction, a substituted 2-cyanopyridine has been identified among the reaction products in each case.

If, as postulated in our earlier paper (7), we assume that the formation of these substituted pyridines occurs through a Diels–Alder type of mechanism with spontaneous dehydrogenation of the primary adduct, then each reaction would be predicted to give rise to two isomeric substituted 2-cyanopyridines. The table below gives, in the first column, the formula of the compound reacted with cyanogen and in the second and third columns, the formulas of the two predicted isomeric products.

(i)  Isoprene	 2-Cyano-4-picoline	 2-Cyano-5-picoline
(ii)  Chloroprene	 5-Chloro-2-cyanopyridine	 4-Chloro-2-cyanopyridine
(iii)  2-Methylpentadiene	 6-Cyano-2,4-lutidine	 6-Cyano-3,5-lutidine

In the experimental section of this paper, the compound given in the second column of the above table was, in each case, identified among the products of each respective reaction. In the case of the first two reactions, evidence was also obtained for the presence of an isomer but its structure was not investigated. As in the previous paper (7), no attempt was made to identify hydrogen in the off-gas from the reaction.

In the literature on the Diels–Alder reaction (11), it is reported that dienophiles will not add to halogenated dienes of the structure Cl−C=C−C=C or C=C (Cl)−C (Cl)=C, but will add to dienes of the structure C=C (Cl)−C=C if there are no other chlorine atoms in the molecule. Our results with cyanogen and chloroprene on the one hand, and hexachlorobutadiene on the other, are in accord with this.

The reactions of cyanogen with the 1,3-dienes mentioned in this paper are thus seen to be not inconsistent with predictions based on a postulated Diels–Alder mechanism, with spontaneous dehydrogenation of the primary adduct at the temperature of the reaction.

The results of this research have been covered in a recent patent application (8).

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THE PREPARATION OF CYANOGEN CHLORIDE[1]

By H. W. Barnett,[2] R. G. Davis,[3] and R. P. Graham[4]

Abstract

A detailed description is given of a laboratory method for the preparation of cyanogen chloride. The method involves the action of chlorine on a solution of zinc sulphate and sodium cyanide, the reaction being carried out under carefully controlled conditions. The procedure described has been found to give a pure product in yields close to 70% of the theoretical.

Introduction

Cyanogen chloride, a colourless gas at normal temperatures, was apparently first prepared about 150 years ago by Berthollet (1).

Some years ago Jennings and Scott (9) and Mauguin and Simon (13) reviewed the early studies on the preparation of cyanogen chloride, all of which involved, as do the methods in use today, the reaction of chlorine with hydrocyanic acid or with other cyanides. Jennings and Scott proposed a method using carbon tetrachloride, rather than water, as a diluent to dissipate the heat of reaction; the use of materials such as carbon tetrachloride in this connection has been the subject of patents (3, 6, 14, 18, 19).

A number of synthetic procedures have been described in the literature in addition to those referred to above. A method, first used by Gay-Lussac, involving the chlorination of an aqueous solution of hydrogen cyanide has been further studied (13, 16) and patented (5). Cyanogen chloride has been prepared by the union of gaseous chlorine and hydrogen cyanide (7, 20) and by the electrolysis of an aqueous solution containing hydrochloric acid and either hydrocyanic acid or sodium cyanide (12, 13). Preparations have been reported in which sodium chlorate* or sodium hypochlorite (12) have been used in reaction with an aqueous solution of sodium cyanide and hydrochloric acid.

Held (4) is credited with being the first to suggest the action of chlorine on a solution of zinc sulphate and alkali cyanide as a means of preparing cyanogen chloride. This procedure, which was designed to prevent the formation of paracyanogen, has been regarded unfavourably by certain workers (9, 16), but has been recommended by others (2, 10, 11, 21). The present writers have

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* *Anon. Pub. Health Repts. 37 : 2744-2747. 1922.*

employed the principle of this method, using the apparatus and procedure described below, to obtain good results.

Apparatus

The reaction flask, *A* (Fig. 1), is a 2 litre round-bottomed flask fitted with an inlet tube, *C*, for chlorine, a thermometer well, a stirrer, and a distillation outlet. Chlorine from a cylinder is passed through concentrated sulphuric

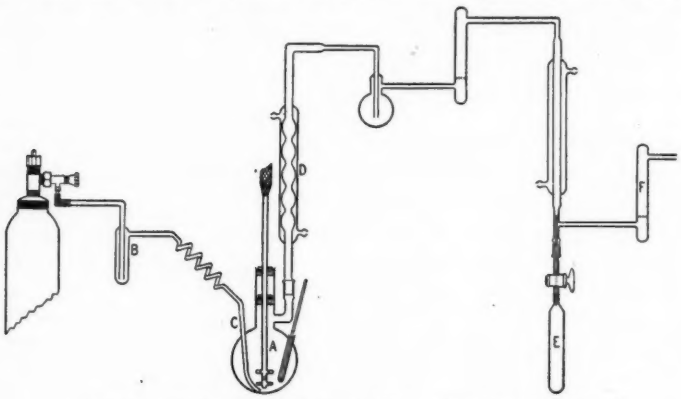

FIG. 1. *Apparatus for the preparation of cyanogen chloride.*

acid (20) in the trap *B* (the use of water in this gas flow-rate indicator may lead to the plugging of the chlorine inlet tube in the reaction flask, *A*, by chlorine hydrate) and a glass spiral to absorb vibrational shock, and then is admitted to the reaction flask through the inlet tube, which is fitted at its end with a sealed-in sintered glass disk to distribute the gas immediately below the blades of the agitator. Attached to the shaft of the agitator are two small graphite disks, which bear on larger graphite disks sealed* in the neck of the flask. These graphite disks, carefully machined, were found to provide excellent self-lubricating stirrer bearings. The arrangement may be made essentially gas-proof by keeping the upper bearing covered with water. Violent agitation in the reaction flask is provided by rotating an efficient three-bladed stirrer at 2000 r.p.m.

To the distillation outlet of the reaction flask there is connected, by means of a ground glass joint, an Allihn condenser, *D*. The outlet from this foam-breaking condenser leads to a 250 ml. round-bottomed flask, which serves as a foam trap, and thence to two purification and drying tubes (150 by 25 mm.) connected in series. (Only one tube is shown in Fig. 1.) These tubes contain a packing of marble chips and calcium chloride** (12, 16) supported by a

* *'Sauer-eisen', an electrical resistor cement manufactured by the Technical Products Company, Pittsburgh, Penn., was found to be very satisfactory for the glass-to-carbon seals. A mercury seal is unsatisfactory because the attack of chlorine on mercury causes fouling of the seal.*

** *If line blockage occurs owing to caking of the calcium chloride, towers containing marble and activated alumina (indicating type) may be used.*

sealed-in sintered glass disk. The outlet from the train (to remove acid and water) is sealed to the top of a Liebig condenser, the latter being connected to the receiver, *E*, by means of a ground glass joint. A drip-tip outlet, ring-sealed to the condenser tube, passes through the ground joint and through the 4 mm. bore of a stopcock which is sealed to the ignition tube receiver. This arrangement permits the use of the receiver as a storage container for the cyanogen chloride after distillation, and at the same time eliminates any contact of the liquefied product with the stopcock lubricant. The outlet to the air is fitted with a calcium chloride – soda lime tube, *F*.

The reaction flask is clamped in an ethylene glycol – water bath (40% ethylene glycol by volume) contained in a well insulated Pyrex jar. The bath is fitted with a 1000 w. coil heater (encased in a Pyrex shield), a low range alcohol thermometer, and an efficient agitator. Lowering of the bath temperature, when necessary, is effected by the addition of solid carbon dioxide.

The cooling liquid for the condensers consists of an 1 : 1 (by volume) mixture of motor oil (S.A.E. No. 10) and kerosene. It is circulated at the rate of approximately 2 litres per minute by means of a gear-type oil pump, and is cooled by passing it through a glass coil immersed in a dry ice – alcohol mixture contained in a Dewar flask. A T-bore stopcock inserted in the system permits circulation through either the Allihn (foam-breaking) condenser or the Liebig condenser separately, or through both condensers simultaneously. A thermometer is inserted in the circulation system in the return lead between the condensers and the pump. The condensers and all connecting tubing are, wherever possible, lagged with asbestos pulp for thermal insulation. Rubber connections in the circulation system swell appreciably during use; the use of neoprene may be more satisfactory.

Procedure

A solution is prepared by dissolving 147 gm. of sodium cyanide in 300 ml. of water (filtering if necessary) and is added slowly with constant stirring (under a hood) to a solution containing 216 gm. of zinc sulphate heptahydrate in 450 ml. of water.* If necessary a very small additional amount of sodium cyanide is added after the mixing to dissolve any remaining precipitate of zinc cyanide. The resultant solution (which is 4 *M* in sodium cyanide and 1 *M* in zinc sulphate,** or 1 *M* in sodium tetracyanatozincate, $Na_2Zn(CN)_4$, and 1 *M* in sodium sulphate) is filtered and transferred to the reaction flask.

Solid carbon dioxide is added to the ethylene glycol – water bath until the temperature in the reaction flask reaches 5° C. Chlorine at a rate of about

* *The quantities of reagents specified are sufficient for a theoretical yield of 184 gm. of cyanogen chloride. Using a 6 litre reaction flask, one of the authors (H.W.B.) has a number of times successfully carried out the synthesis on three times as large a scale, using essentially the same apparatus and procedure described in this paper.*

** *Held (4) recommended the use of 1/3 mole of zinc to every 4 moles of cyanide, but later workers (10, 13, 21) have preferred a ratio of 1 mole of zinc to 4 of cyanide. Zappi (21) chlorinated a solution that was 0.77 M in potassium cyanide, and Klemenc and Wagner (10) one that was 1.54 M in potassium cyanide. Mauguin and Simon (13), who used sodium cyanide in place of the potassium salt, employed a number of concentrations of cyanide, including 1 and 2 M.*

200 to 300 bubbles per minute (through 8 mm. tubing) is then admitted to the vigorously agitated reaction mixture, and the addition of dry ice is regulated so that the temperature in the reaction flask is maintained between 0° and 5° C. An appearance of milkiness in the reaction flask indicates the initiation of an exothermic reaction, possibly $Na_2Zn(CN)_4 + 2Cl_2 \rightarrow Zn(CN)_2 + 2NaCl + 2CNCl$ (13). As chlorination proceeds, the mixture becomes more viscous and there appears an increasing amount of white precipitate (presumably zinc cyanide) in the reaction flask, and froth on the surface of the liquid. At this stage the rate of chlorination may be increased provided that the temperature in the reaction flask does not rise above 5° C. (during the last stages of the chlorination it is desirable that the rate be decreased to 200 to 300 bubbles per minute). When the mixture becomes almost a thick paste, the exothermic reaction proceeds with considerable vigour, and it is necessary to cool the bath, which may conveniently be done by the addition of solid carbon dioxide, to approximately −25° C. in order to maintain the temperature within the reaction flask between 0° and 5° C. A thinning of the mixture within the reaction flask due to a decrease in the amount of white precipitate present marks the last stage of the exothermic reaction and the start of an endothermic reaction, possibly $Zn(CN)_2 + 2Cl_2 \rightarrow ZnCl_2 + 2CNCl$ (13). At this stage it may be necessary to turn on the heating unit in the ethylene glycol – water bath to raise the temperature of the bath somewhat in order to maintain the temperature within the reaction flask at 0° to 5° C. As the endothermic reaction proceeds, the mixture progressively becomes thinner, and both the quantity of white precipitate and the foaming of the liquid in the reaction flask decreases. The completion of the reaction is marked by the complete disappearance of the precipitate, and it is very important that chlorination be stopped promptly at this point.

Care must be taken throughout the chlorination procedure that the agitator in the reaction flask is not stopped at any time, otherwise chlorine may escape from the solution and pass over into the scrubbing and condensing system.* Under-chlorination will leave a residue of zinc cyanide in the flask that may cause severe foaming during the distillation. Over-chlorination will result in a product contaminated with chlorine, necessitating a later purification procedure, e.g., distillation from metallic antimony or zinc, fractional distillation under reduced pressure (10), contact with mercury (2, 9, 16) or arsenic (17, pp. 188-191), or with an aqueous suspension of zinc oxide or yellow mercuric oxide (16) or with one of calcium carbonate and zinc oxide at 0° C. (10, 21) followed by drying and distillation.

Distillation of the cyanogen chloride from the reaction mixture is carried out in the following manner. By means of the circulating pump, the kerosene–oil solution is circulated through the Liebig condenser at a temperature of 0° to 3° C. The receiver is maintained at −20° C. by immersing it in a

** Experience with this synthesis has shown that the rate at which cyanogen chloride is produced may be greatly increased by maintaining a positive pressure of chlorine in the reaction flask during the first stage of the chlorination procedure; this is accomplished by disconnecting the Allihn condenser and blocking the outlet from the flask.*

freezing mixture of solid carbon dioxide and alcohol contained in a Dewar flask. The temperature of the ethylene glycol bath is raised slowly by means of the heating unit. When the temperature of the reaction flask reaches 8° to 9° C. the cyanogen chloride begins to distil, and comes over fairly rapidly when the temperature has reached 13° C.

If foaming occurs and the froth threatens to be carried over into the line, the kerosene–oil solution at 0° to 3° C. is circulated through the foam-breaking condenser. This procedure retards distillation, however, and should be carried out only if necessary. It should be mentioned that the presence of 'Aerosol OT' in the reaction flask decreases the tendency toward foaming.

The distillation is continued by regulating the supply of heat to the reaction flask so that distillation proceeds smoothly at a convenient rate. It is necessary to raise the temperature of the reaction flask to 40° to 45° C. toward the end of the distillation procedure in order to remove the last of the cyanogen chloride from the reaction mixture. When distillation is complete, the receiver is removed from the condenser, the stopcock is closed, and the container is stored in a Dewar flask containing a solid carbon dioxide – alcohol mixture.

If the procedure is carried out properly, a clear colourless liquid, or white solid when frozen, is obtained. The yield was 60 to 70% of the theoretical amount. It has been reported that polymerization of cyanogen chloride to the white solid trimer, cyanuryl chloride, $(CNCl)_3$, is hastened by the presence of moisture (17, pp. 188–191), hydrochloric acid (9, 16, 20), and possibly chlorine (17, pp. 188–191, but cf. 16), but that if the pure material is kept dry and stored in glass, it remains stable for many months (16). The product prepared by the method outlined above showed no evidence of polymerization until it was some months old.

Because of the violently toxic nature* of cyanogen chloride, its synthesis should be carried out under a hood equipped with a fan giving rise to an exceptionally high flow of air. It is recommended that operators of the apparatus wear adequate respirators.

Acknowledgments

The authors are indebted to the Proofing Section of the Chemical Warfare Laboratories and to Messrs. A. S. Tulk and E. T. Clarke of McMaster University for helpful suggestions regarding the construction and operation of the apparatus described.

Acknowledgment is made to the National Research Council of Canada for the financial support accorded and for the award of a Bursary to one of us (R. G. D.).

* *Cyanogen chloride is a systemic poison and paralyzant (8, pp. 10 and 37); exposure to it in a concentration of 0.4 mgm. per litre for 10 min. is probably lethal (15, p. 175). Its toxicity has been assessed as 13.5 on the basis of chlorine = 1.0 (8, p. 170). In addition to its toxic action, cyanogen chloride is a lachrymator; the concentration required to produce a lachrymatory effect in a few minutes has been given (15, p. 175; 17, pp. 188-191) as 0.0025 mgm. per litre or 1 p.p.m.*

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DIMETHYLDINITROÖXAMIDE[1]

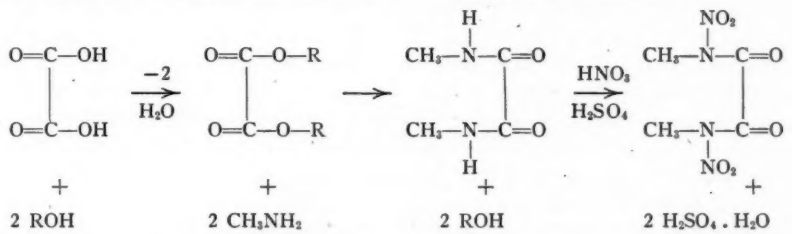
O. C. W. ALLENBY[2] AND GEORGE F. WRIGHT[3]

Abstract

A practical low-cost method is described for the preparation of the explosive dimethyldinitroöxamide. Dimethyloxamide is prepared in 94% yield from an oxalic ester and methylamine, and then is nitrated in 98% yield with slightly more than the requisite amount of nitric acid. The nitrating acid can be recovered safely. The optimum yield is obtained when the waste acid has the composition sulphuric acid monohydrate.

The explosive dimethyldinitroöxamide was first prepared by Franchimont (1, 2, 3) in 93 to 97% yield by treating dimethyloxamide with five times its weight of absolute nitric acid. Thiele and Meyer (6) used rather less nitric acid and supplemented it by addition of sulphuric acid. Their yields of good material were almost theoretical.

In connection with our directive in 1940 to investigate practical methods of nitramine explosive manufacture, we sought the most economical method for preparing dimethyldinitroöxamide. The following formulation



indicates these economies must be applied firstly to dimethyloxamide formation, and secondly to its nitration.

Dimethyloxamide has been prepared from ethyl oxalate and methylamines (8, pp. 50-51) or a mixture of methylamines (9, 10, pp. 443-464) but we chose instead to use amyl oxalate, because this ester can be prepared simply by azeotropic distillation of oxalic acid and the alcohol (7, pp. 337-339). For example, we obtained an 85% yield of amyl oxalate in three hours by withdrawing the water from a decanter as fast as it co-distilled with the amyl alcohol which returned to the reaction vessel.

This amyl oxalate is then added slowly to carbon tetrachloride previously saturated with methylamine and maintained in saturation during the addition. The yield of dimethyloxamide of nitration grade constitutes 94% of the theoretical.

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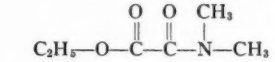
Pure monomethylamine is not easily available, but an ordinary methanol–ammonia reactor yields, after ammonia is stripped off, a mixture of 88.6% monomethylamine, 6.86% dimethylamine, and 4.78% trimethylamine together with methanol. When the mixture was used to replace the pure monomethylamine in the above procedure, an unsatisfactory product was obtained, which probably contained ethyl dimethyloxadamate. This oily substance



was found by Hofmann (4, 5) to be the contaminant when he attempted a similar preparation with mixed amines.

This impurity was eliminated simply by adding the amyl oxalate to a large excess of the methylamines, which also acted as the reaction medium. Because of its preponderance, the monomethylamine reacted by preference; and the large amine excess precluded any half-ammonation which might yield products like ethyl dimethyloxamadate. When the reaction was complete, the excess amines were distilled off and the residue washed with carbon tetrachloride to remove amyl alcohol (which should be returned to the esterification reaction). The yield of dimethyloxamide by this method is 86% of theoretical and its melting point, 214° to 215° C., indicates it to be entirely suitable for nitration. The material will, however, be unsuitable for nitration if oxidizable amyl alcohol is not entirely washed out, or if the original amine mixture contains more than 2 to 3% of ammonia. It is not difficult, however, to ensure an amine mixture free from ammonia because of the differences in properties. Thus the solubility of methylamine in carbon tetrachloride at 25° C. is 1.1%, while that of ammonia is 0.003%. Such a differential cannot be used directly, since the presence of methanol vitiates this favourable ratio, but it serves to show that purification systems to remove ammonia can easily be devised.

The nitration method of Thiele and Meyer is clearly not the ideal practical procedure, firstly because it is wasteful of nitric acid, and secondly because the acid mixing is carried out with the dimethyloxamide in solution. This would invite decomposition unless heat removal were extremely efficient.

We found that a 98% yield of dimethyldinitroöxamide could be produced using slightly more than the theoretical quantity of nitric acid in a mixed acid prepared from 60% nitric acid and 20% oleum. The mixed acid required for one mole of dimethyloxamide contains 2.1 moles of 100% nitric acid, 5.51 moles of 100% sulphuric acid, and 3.15 moles of water. Upon completion of nitration, the remaining acid will therefore be almost exactly sulphuric acid monohydrate. This condition is necessary for attainment of maximum yield. It may be seen from Fig. 1 that the yield falls sharply when the water content of the mixed acid deviates slightly from the optimum. It is fortunate that the optimum acid mixture is the cheapest that can be prepared from common ingredients.

The crude explosive is pure according to melting point criteria, but we usually crystallized it from carbon tetrachloride containing a little calcium carbonate in order to ensure freedom from acid and water, and also to deposit

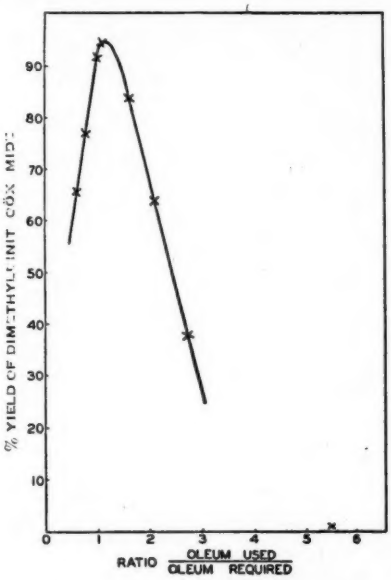


FIG. 1. *Nitration of dimethyloxamide.*

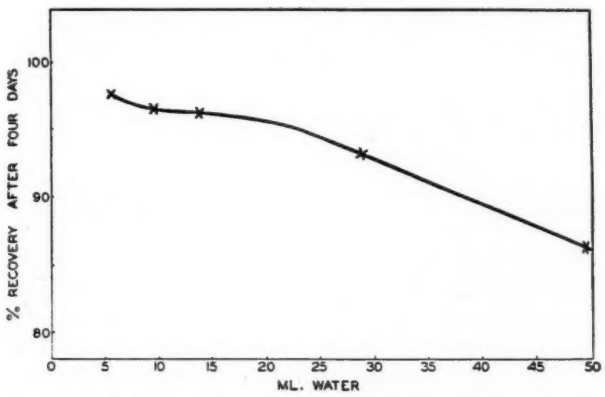


FIG. 2. *Hydrolysis of dimethyldintiroöxamide.*

on it a trace of paraffin in order to make it water repellant. This may be advisable because of its tendency toward hydrolysis by water. Fig. 2 shows that the rate of this hydrolysis depends on the amount of water present; in

other words the substance is stabilized by its own decomposition products. The explosive is non-hygroscopic, and destruction by water hydrolysis ought not be more severe than with the common explosive nitroguanidine, which has similar properties.

Dimethyldinitroöxamide cannot be used as a pourable explosive since it decomposes at its melting point of 124° C. Its power as measured in the ballistic mortar and Trauzl block is 1.05 times that of T.N.T. The impact sensitiveness of the pure explosive is equivalent to that of T.N.T.; a film coating (less than 0.1%) of paraffin reduces this sensitiveness to 0.9 that of T.N.T. It is, however, more sensitive than T.N.T. to sympathetic detonation from 60% dynamite. The rate of detonation of dimethyldinitroöxamide is 4900 to 6760 m. per sec., depending on the density of 1.03 to 1.42. Its heat of formation is 74.5 kcal. per mole, based on a heat combustion of −508.4 kcal. per mole. It forms a pourable mixture with setting point 75° C. when mixed in equimolar amount with picric acid. The rate of detonation of this mixture is 6680 to 7500 m. per sec., depending on densities of 1.41 to 1.59.

Experimental*

Dimethyloxamide from Pure Methylamine

A 12 gal. stainless steel vessel was equipped with a wide-sweep stirrer, internal cooling coil, and external spray water cooling. Into this vessel was introduced 3.2 U.S. gal. of carbon tetrachloride which was saturated with methylamine by means of a gas inlet at the bottom. By means of stirring and cooling, the temperature was held at 20° C. while 12.8 lb. of dibutyl oxalate (used interchangeably with the amyl ester) and 4.05 lb. of methylamine were added over a four hour period. After one hour's subsequent stirring, the slurry was centrifuged and washed with one gallon of carbon tetrachloride. The yield of 7 lb. of nitration-grade dimethyloxamide (m.p. 210° to 211° C.) was 94% of theoretical on the ester basis.

Dimethyloxamide from Mixed Methylamines

A mixture of the amines and methanol in the proportions 1210 gm. (39.4 moles) of methylamine, 93.5 gm. (2.08 moles) of dimethylamine, 66.5 gm. (1.13 moles) of trimethylamine, and 285 gm. (9.2 moles) of methanol was condensed into a flask cooled to −15° C. and equipped with dropping funnel, stirrer and reflux condenser cooled to −30° C. To this stirred liquid was added, over 25 min., 230 gm. (1 mole) of diamyl oxalate. After several hours, the mixture of amines was allowed to distil off, and the residue washed on a filter with five 300 cc. portions of carbon tetrachloride. The yield of dimethyloxamide melting at 214° to 215° C. was 101 gm. or 86% of the theoretical amount. A further 6.2 gm. of material unsuitable for nitration was obtained from the wash liquors.

* *All melting points are corrected against known standards.*

It is obvious that the latter procedure can be adapted to the use of pure methylamine, although the first procedure cannot be used with mixed amines.

Nitration of Dimethyloxamide

A mixture of 12.6 lb. (68 moles) of 75% nitric acid and 39 lb. (176.8 moles) of 98% sulphuric acid (or its equivalent in 58% nitric acid and 20% oleum) was mixed carefully to ensure a low nitrous acid content and then cooled and maintained at 30° C. in a 12 gal. stainless steel kettle equipped with external spray cooling and a stainless steel stirrer with four staggered blades 4 by 6 in. which cleared the kettle wall (13 in. diameter) by only ½ in. This stirrer was driven by reduction gear at 100 to 120 r.p.m. while 8.63 lb. (33.7 moles) of dimethyloxamide was added over one hour. The heavy slurry was stirred two hours longer; the mixture will evolve gas if the temperature rises much above 30° C.

The slurry was filtered without difficulty through glass cloth. The precipitate was then transferred portionwise into 6 U.S. gal. of stirred cold water, refiltered and washed with 10 U.S. gal. of water until neutral to bromcresol green. This product was air-dried to weigh 15 lb. (98% of theoretical on dimethyloxamide basis) and melt at 124° C.

The spent-acid filtrate, consisting of sulphuric acid monohydrate with the 5% nitric acid excess, usually warmed up during filtration, unless it was cooled, and evolved some nitrogen oxides. Dilution of this liquor with twice its volume of water precipitated 1.9% of the theoretical yield of dimethyldinitroöxamide (therefore the remainder of a 100% yield) as a tan powder, m.p. 122° to 124° C.

In practice this small amount of material would probably be sacrificed by heating the undiluted liquor. A smooth easily regulated fume-off of nitrogen oxides thus occurs, leaving the sulphuric acid free from explosive and nitric acid and thus clean enough for subsequent concentration or fortification. This denitrated sulphuric acid does however contain a small amount of non-explosive organic material.

Crystallization of Dimethyldinitroöxamide

When 15.8 lb. of air-dried explosive was dissolved in 12.6 U.S. gal. of boiling carbon tetrachloride containing 5 gm. of suspended calcium carbonate, a 91% recovery was obtained by cooling. The melting point of 124° C. was not raised by this crystallization, which was probably unnecessary in view of the purity of the crude material. However, the 1.5 lb. of material recovered by evaporating the solution medium melted at 123.5° to 124° C. The addition of 0.16 lb. of paraffin to the hot carbon tetrachloride caused a more rapid crystallization which began after slight cooling below the boiling point and thus tended to clog the hot filter unless it was adequately heated. The resulting crystals were strongly water repellant, but the bulk density was decreased from 0.8 to about 0.6.

Hydrolysis and Thermal Stability of Dimethyldinitroöxamide

The data recorded in Fig. 2 were obtained by shaking 5-gm. portions suspended in various amounts of distilled water in air-tight tubes at 25° C. for four days. They indicate, by extrapolation toward minute amounts of water, that hydrolysis due to dampness would be negligible. A sample of dry material at 70° C. for three weeks in a closed tube showed no decrease in melting point and no volatile acidity to bromcresol green or congo red papers. No evolution of nitrogen oxides from the dry explosive is detectable after four hours at 100° C.

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OSMOTIC PRESSURE MEASUREMENT AND THE INSTABILITY OF HIGH POLYMERS[1]

By A. F. Sirianni,[2] L. M. Wise,[2] and R. L. McIntosh[3]

Abstract

In attempting to obtain accurate osmotic data in the low concentration range, it was found that the results were influenced by the diffusion of solvent from the cell through the membrane gasket. This behaviour was prevented by auxiliary sealing in a cell of new design, and results obtained with the improved cell are compared with those obtained with previous types of osmometer. A partial re-examination of the influence of preparation of the membrane was made in order to check results reported by Robertson, McIntosh, and Grummitt, and the different behaviour of caustic swollen and water swollen cellophane membranes has been confirmed, although quantitative agreement for water swollen membranes between the two investigations was not obtained. Using caustic treated membranes the molecular weight of a polyvinyl acetate sample was found to be the same within experimental error in three solvents.

Further results on the changes in intrinsic viscosity and molecular weight brought about by ageing at elevated temperatures in the presence and absence of oxygen are reported for polyvinyl acetate and polymethyl methacrylate. It appears that oxygen is necessary to bring about molecular weight changes, and the degradation is due to scission of the chains at weak points. The evidence also suggests that changes in molecular shape may occur, since intrinsic viscosity values altered in some cases without evidence of molecular weight variation. This last observation is apparently outside the limits of error in reproducing osmotic pressure values.

Part I

Osmometry

Introduction

It has been known for some time that solutions of high polymers are not entirely stable when stored over long periods of time. Several instances of instability in solutions of high polymers are recorded in the literature. Mead and Fuoss (23) reported changes in viscosity of solutions of polyvinyl chloride in methyl amyl ketone and cyclohexanone. Wehr (34) states that the stability of solutions of polyvinyl chloride in several solvents depends on the degree of saturation of the polymer, the light intensity, and the presence of catalysts. Blaikie and Crozier (4) found that solutions of polyvinyl acetate in glacial acetic acid at 160° C. initially decreased in viscosity and then increased. Decreases in viscosity on standing have also been noted by Jirginson (16) for solutions of gelatin in water, by Bartell and Cowling (2) for alkali cellulose and by Ott (30, Chap. VIII) for pure cellulose. In many cases (2; 4; 30, Chap. VIII) it has been noted that the presence of oxygen

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Contribution from the Department of Chemistry, McGill University, Montreal, Que., and Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1543.

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affects the degradation. Naunton (29) showed that rubber solutions exposed to light and oxygen slowly absorbed oxygen, while the viscosity of the solution decreased.

An investigation of the instability of solutions of polyvinyl acetate, polystyrene, and polymethyl methacrylate in three solvents, bis(2-chloroethyl) ether, nitrobenzene, and bis(2-chloroethyl) sulphide by Morrison, Holmes, and McIntosh (26) showed that viscosity changes were dependent on the presence of impurities, such as oxygen and ferric salts.

However, on account of the theoretical limitations of the viscosity method, it was impossible to decide definitely whether the viscosity changes were due to changes in the molecular weight of the polymer or to variation in such other factors as (*a*) the degree of solvation of the polymer, (*b*) the orientation or configuration of the macromolecules in solution, (*c*) the chemical nature of the polymer. Osmotic measurements, which theoretically furnish more absolute data, were therefore determined on some of the aged samples (21) and showed that a definite molecular weight change did take place.

The present work was undertaken as a continuation of the studies on the ageing of polymers under varying conditions. During this work, difficulties in osmotic practice came to light. Attempts were made to correct these inadequacies. It is probable that the difficulties discovered were present undetected in the apparatus of other workers, and their probable influence on the results of other workers has therefore been investigated in a preliminary manner.

Towards the beginning of this work, Robertson, McIntosh, and Grummitt (32) showed that, for the system polyvinyl acetate in acetone, osmotic pressures determined using swollen cellophane membranes, prepared by the method of Carter and Record (6), and using cellophane membranes that had been treated with sodium hydroxide, yielded different results. These differences are not explicable as due to imperfectly semipermeable membranes. There is evidence in the literature that this behaviour is a specific case of a more general phenomenon. Fuoss and Mead (9) suggest that a membrane is not suitable unless it is swollen by the solvent employed. Such an explanation is not far different from the explanation proposed by Robertson, McIntosh, and Grummitt (32), which presumes that adsorption of polymer at the membrane is prevented by preferential adsorption of solvent.

Unfortunately, the dynamic osmometer used by Robertson *et al.* could not be used for very low osmotic pressures and, consequently, required a long extrapolation to infinite dilution for the curve osmotic pressure/concentration versus concentration (i.e., π/C vs. C). It was therefore impossible to determine definitely whether the π/C versus C curves for the two types of membranes yielded identical intercepts and thus identical values for the molecular weight. This question was therefore reinvestigated using a modified type of osmometer. At the same time, several other points of fundamental interest have been reinvestigated.

The work reported here is therefore broadly divided into two parts, the first describing the construction of the osmometer and the investigation of membrane preparation and other fundamental points, and the second dealing with the results obtained in the continuation of the investigations on the ageing of polymers.

Experimental

The Osmometer

In designing a suitable osmometer, several factors must be considered:

(1) There must be no interaction between the materials of the osmometer and the solvents or polymers used.

(2) It must be free from leaks.

(3) The presence of bubbles should be easily recognizable and the bubbles easily removable.

(4) The membrane should be held in place as rigidly as possible, since the apparent rate of approach to equilibrium depends on the rigidity of the membrane (7).

(5) On account of the high molecular weights of the polymers and the consequently low osmotic pressures to be measured, a high degree of accuracy is required. Since the π/C versus C curve must be extrapolated to infinite dilution, determinations must be possible on very dilute solutions.

(6) The osmometer should be as rapid in operation as possible.

Osmometers generally may be divided into two classes, dynamic and static. In the dynamic type (5, 33) the flow of solvent across the membrane toward the solution side is opposed by an externally applied pressure, and that pressure determined which just stops the flow of solvent. In the static method (7) the height of liquid set up in a vertical capillary on the solution side is measured. The dynamic type of osmometer, used by Robertson, McIntosh, and Grummitt (32) and by McIntosh and Morrison (21), proved tedious in operation and required a long extrapolation to infinite dilution.

The osmometer originally constructed in the present work was based on the combined static and dynamic osmometer designed by Montonna and Jilk (25), Fuoss and Mead (9), and Flory (7). It consisted of two metal plates, each containing a shallow well surrounded by a flat ring $3\frac{3}{4}$ in. outside diameter. The well contained a series of concentric ridges to support the membrane. The two plates were bolted together over the membrane, which was thus presumed to behave as a gasket, between the flat rings, to seal the osmometer. Each well led to a vertical capillary of 0.5 mm. bore, in contrast to previous designs in which one well led to a capillary tube and the other to a wide tube.

Such an osmometer proved unsatisfactory. The levels in both capillaries dropped simultaneously, irrespective of the external pressure of the thermostating liquid, indicating the presence of a leak. Intensive investigation of several modifications showed that the membrane does not form a satisfactory gasket. Carter and Record (6) arrived at a similar conclusion and Flory (7) states that his cell may have been leaking, but does not locate the leak at the

sealing face. Fuoss and Mead (9) state that, with solvent in both compartments of the osmometer, a difference of at least 1 mm. is observed between the capillary levels. Lossing (18) reports a similar 'asymmetry', whose magnitude can be altered by tightening the bolts about the cell. Nevertheless, the observation of leakage is in contradication to most of the recent literature (3, 7,10). It is therefore proposed to present in some detail the experimental evidence.

The criterion of the existence of leakage lay in whether the liquid levels in the capillaries of a thermostatically controlled cell remained constant over a period of several hours. Conventional tests, such as immersing the osmometer in water and applying air pressures up to 30 lb. per sq. in., proved inadequate, since an osmometer, while appearing free from leaks by this test, still leaked when filled with solvent. The leak was definitely located at the membrane by replacing the membrane with a sheet of 'Composition' metal foil (Pb 97.5%, Sn 0.5%, Sb 2%) of about the same thickness and compressibility as the membrane. The liquid levels remained constant over a period of six hours, except for a drop of 0.015 cm. per hr. from evaporation from the capillaries. Nevertheless, when the metal foil was replaced with a cellophane membrane the usual drop in the levels of 0.2 to 0.6 cm. per hr. was observed. A perfect imprint of the sealing face was invariably found on the membrane. Furthermore, membranes of denitrated collodion, much thicker than cellophane membranes, gave still more rapid leakage when installed in the osmometer. It therefore appears that no mechanical leak existed, but that diffusion took place directly through the membrane.

While several methods of preventing the leakage are undoubtedly feasible, only the one will be described that was adopted, because it gave greatest satisfaction and involved the least alteration of the general design.

On one half-cell, the sealing ring was lowered 0.01 in. below the tops of the ridges in order to accommodate a gasket of 'Composition' metal foil. At the outer edge of the ring on one half-cell was machined a second ring $\frac{1}{8}$ in. wide and raised 0.007 in. above the first ring. This second ring exactly matched a groove in the sealing face of the other half-cell $\frac{1}{8}$ in. wide and 0.007 in. deep (Fig. 1). In practice the membrane fitted inside the ridge and groove system, while a layer of 'Composition' foil 0.01 in. thick was placed over the whole sealing face and sealed at the ridge and groove. The two half-cells were clamped together by means of eight $\frac{3}{16}$ in. bolts around the edge of the cell.

The wells to contain solvent and solution were constructed as described by Robertson, McIntosh, and Grummitt (32), with drill holes leading to the bottom for filling and draining purposes. The tops of these drill holes were initially closed by means of needle valves, consisting of tapered steel plugs fitting into brass cones, tapered at a slightly different angle. Such a system could not be made consistently leak proof. The steel plugs were therefore coated with solder, which was machined to approximately the same taper as the plug. This soft tip gave a vacuum tight seal. The capillaries (0.5

mm. ± 1%) were connected to the wells through Fernico bushings (9). Evaporation from the ends of the capillaries was decreased to 0.015 cm. per hr. by leading the ends over thermostatically controlled bulbs of solvent. It was not possible to eliminate evaporation completely.

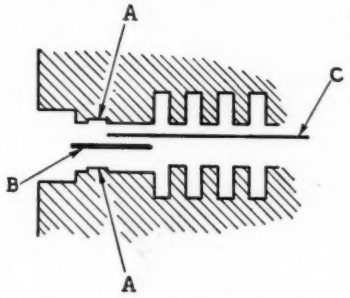

FIG. 1. *Sealing system. A. Ridge and groove system. B. 'Composition' foil. C. Membrane.*

. A photograph of a slightly modified form of this osmometer is shown in Fig. 2. It differs only in being provided with a flooding ridge to facilitate the installation of membranes.

The assembly of the cell required great care to prevent drying and consequent loss of permeability of the membrane. When a flooding ridge was present, the membrane could be kept under solvent in the well formed by the ridge while the cell was being assembled. If the solvent was dense enough to float the membrane, or if no flooding ridge was present, the attention of two persons was required. One half-cell, with the metal gasket, was placed on a slightly inclined support. The membrane was installed while being thoroughly flooded with solvent, the second half-cell put in place, and flooding continued through the filling tubes while the system was being bolted.

Bubbles were partially removed by filling the chambers to just above the membrane and oscillating the cell. Final adjustment of liquid levels was made through the capillaries with a fine pipette. In spite of the utmost care, bubbles frequently manifested themselves after the osmometer was in use, either by actual appearance, or by causing a continuous movement of the liquid levels in excess of that from evaporation. Gee (10) and Flory (7) attributed bubbles to trapped air which could be removed by oscillation. Present observations indicate that this is not entirely the case. Bubbles rarely appeared until the temperature of the cell was raised somewhat by placing it in the thermostat. Furthermore, bubble formation was much more pronounced when a fresh membrane was placed in the osmometer. The difficulty caused by bubbles became progressively worse over a period of months, probably as a result of corrosion, since either remachining the metal or gold plating it reduced markedly the difficulty from bubbles (22). The extent of the difficulty also varied with the solvent used, increasing in the order benzene, chloroform, acetone.

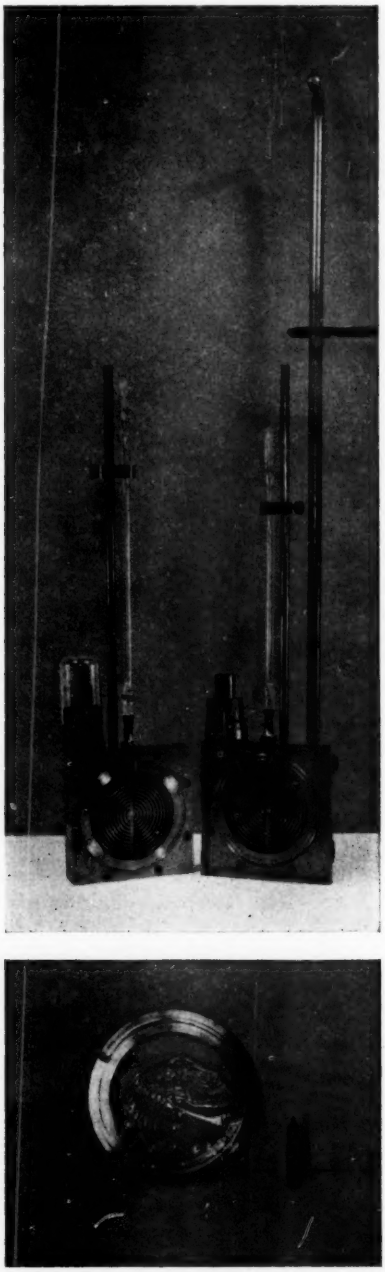

FIG. 2. *Gold plated osmometer. Above—Osmometer. Below—'Composition' foil, membrane and solder-tipped valve plug.*

It appears, therefore, that bubbles, in addition to trapped air, arise from air dissolved in the solvent and adsorbed on the membrane and cell faces. The emergence of this air is probably aided by increased temperature, and the removal of bubbles hindered by rough surfaces such as arise from corrosion of the metal.

In a gold plated osmometer, bubbles were removed by oscillation of the cell during filling and by applying gentle suction at the ends of the capillaries to remove those that subsequently appeared. For unplated osmometers, it was found advisable to warm the filled osmometer for several hours at a temperature 2° to 3° C. higher than the thermostat temperature and then, with the valves open, to oscillate the liquid levels. In all cases, bubble effects were considered absent when the movement of the liquid levels had decreased to that attributable to evaporation (0.015 cm. per hr.).

The osmometer was thermostated at 30 ± 0.001° C. in an oil-bath controlled by a mercury thermoregulator, equipped with a supersensitive relay and a vibrator.

It was found more convenient to use the system as a static rather than a dynamic osmometer.

Careful machining of the plates was required in order that the membrane might be held rigidly. A loosely held membrane had a low apparent permeability.

Membranes

For investigation of the effect of caustic on cellophane membranes (32), both caustic treated and untreated membranes were prepared. For untreated membranes, squares of cellophane No. 600 PT, obtained from Canadian Industries Limited, were first partially freed of plasticizer by being boiled in water for one hour. Circles of the required size were then cut out, allowing $\frac{1}{8}$ in. in diameter for subsequent shrinkage. Final traces of plasticizer were removed by a second boiling in water (19). In order to accommodate the membrane to the solvent the membrane was dipped twice for two minutes in 95% ethanol, stored in 99% ethanol for 12 hr. and then transferred to anhydrous acetone.

For caustic treated membranes, after removal of plasticizer, the membranes were soaked in 2% sodium hydroxide solution for 15 min. In order to accommodate the membrane to the solvent without washing out the caustic, the membranes were dipped for two minutes in distilled water and twice, for two minutes each, in 95% ethanol. They were then placed in 99% ethanol for 15 min. and stored in anhydrous acetone. When a brass osmometer was used with acetone as solvent, it was found that a large downward drift in the liquid levels occurred if more than 2.3 mgm. of sodium hydroxide was contained in the membrane. No such effect was observed for benzene or chloroform, nor for acetone in a gold plated cell.

Intrinsic Viscosities

Intrinsic viscosities were measured at 20 ± 0.02° C. in the ordinary manner by means of an Ostwald type viscometer having outflow times of approximately 72, 76, and 136 sec. for chloroform, acetone, and benzene, respectively.

Materials

The polyvinyl acetate was a commercial product (Gelva V 45 and V 360) supplied by Shawinigan Chemicals Ltd. It was purified by being dissolved in acetone, filtered, precipitated into distilled water, and dried *in vacuo*.

The polymethyl methacrylates were supplied by E. I. duPont de Nemours and Co. (NDR 474, 471, 359). They were dissolved in benzene, filtered, and precipitated into petroleum ether.

The chloroform and acetone were Merck Reagent Grade. They were dried over calcium chloride, distilled, and stored over Drierite. The benzene was Mallinckrodt's Reagent Grade, dried over calcium chloride and stored over sodium wire. The ethanol was Standard Chemical Co. 95%, and the petroleum ether was Mallinckrodt's Reagent Grade, b.p. 30° to 60° C.

Preparation of Solutions and Test for Semipermeability

Solutions were made up by weight. For determination of the tiny quantities occasionally appearing on the solvent side during tests for semipermeability of the membranes, the liquid was run into distilled water and the resultant turbidity estimated with a Fisher A.C. Model Electrophotometer. Where the solvent was immiscible with water, the solvent was evaporated on a steam-bath and the residue taken up with acetone before being mixed with the water. Concentrations as low as 0.001 gm. per 100 cc. could be detected.

Results

Comparison of Osmometers

Since the difficulties encountered in designing a suitable osmometer were such as to make it probable that they were present in osmometers used by other workers, a comparison was made between osmotic pressures determined with the metal-gasketed and with the old types of osmometer. Solutions of Gelva V 45 and V 360 were used with membranes of comparatively low caustic content. The results are shown in Fig. 3. Curves 1 represent determinations with the present, improved osmometer. Curves 2 were determined by Robertson, McIntosh, and Grummitt (32) on identically prepared polymer samples, using a dynamic osmometer with a membrane gasket. Curve 3 was established with the present osmometer without the 'Composition' foil gasket, under the apparently unwarranted hypothesis that the rate of leak was identical on both sides and would not affect the osmotic pressure. The leak (about 0.1 cm. per hr.) masked the presence of bubbles on the solution side, so that most of the results are high. Finally, the capillary on the solvent side was replaced with a large tube to give a true Fuoss and Mead type of osmometer (9). The masking effect of the large tube permitted both

bubbles and leakage to remain undetected. The bubble effect presumably predominated, resulting in the points, shown as triangles, being high, rather than low.

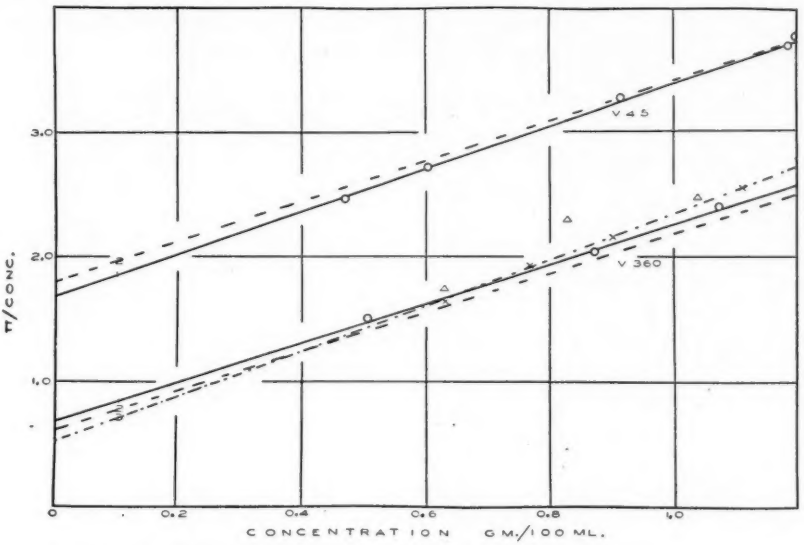

FIG. 3. *Data obtained with improved and conventional type osmometers.*
Curve 1: ————————
Curve 2: — — — — —
Curve 3: — · — · — · — ·

Molecular Weights in Different Solvents

Published osmotic data (11) indicate that the π/C versus C curves for a given polymer in different solvents may have different slopes but identical intercepts and thus yield identical values for the molecular weight. The point is of such fundamental importance that it was reinvestigated with the improved osmometer. The molecular weight of Gelva V 45 in acetone, benzene, and chloroform was determined using a 2% caustic treated membrane. As seen in Table I and Fig. 4, the intercepts, and so the molecular weights, are identical

TABLE I

MOLECULAR WEIGHT OF POLYVINYL ACETATE (GELVA V 45) IN VARIOUS SOLVENTS

Solvent	$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^2} C_2^2\right)_{C_2=0}$	$M_n \times 10^5$	Slope	μ_1
Chloroform	1.87	1.38	3.32	0.377
Benzene	1.84	1.40	1.52	0.427
Acetone	1.82	1.41	1.50	0.439

within 1.5%. It is noteworthy that, in these curves, the negative term $\frac{RTd_1}{3M_1d_2^3}C_2^2$ in Huggins' equation (14) is not negligible and has been included in the calculations. Furthermore, the curves for benzene and acetone are almost identical, while that for chloroform differs markedly in slope. This is reflected in the values of the Huggins' characteristic constant, μ_1 (13).

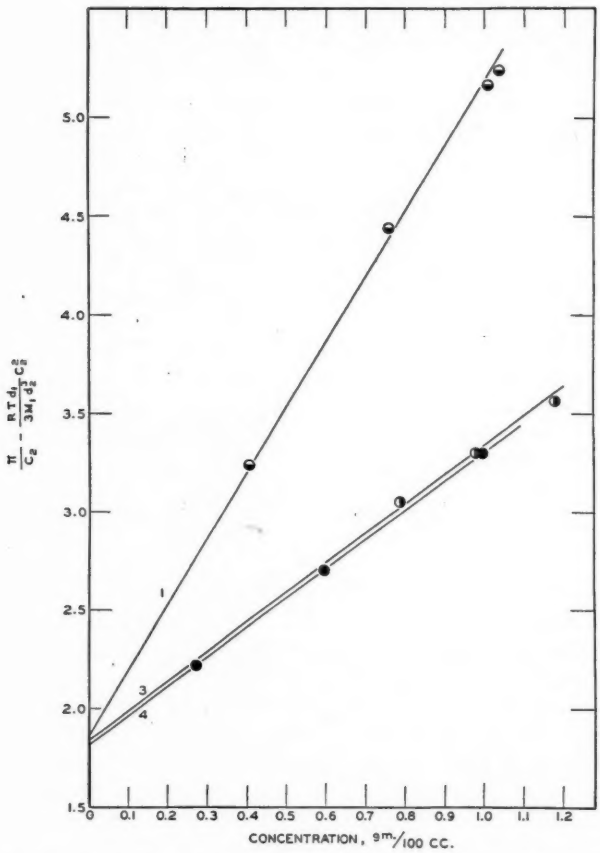

FIG. 4. *Osmotic pressure of Gelva V 45 in different solvents. 1. Chloroform. 3. Benzene. 4. Acetone.*

For comparison, intrinsic viscosities were determined for the same systems. The results are shown in Table II and Fig. 5.

As in the case of the osmotic pressures (Table I), the curves in benzene and acetone are almost identical, while that in chloroform differs markedly. In spite of the marked difference between the curve for chloroform and the other

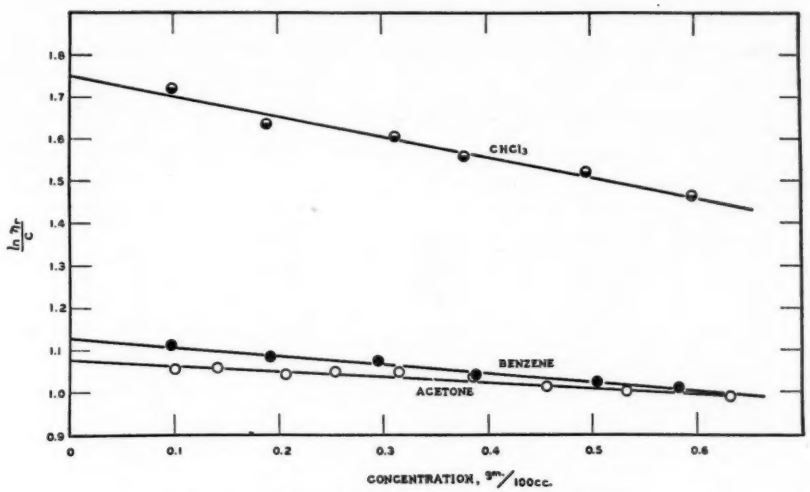

FIG. 5. *Viscosity of Gelva V 45 in different solvents.*

TABLE II

VISCOSITY AT 20° C. OF POLYVINYL ACETATE (GELVA V 45) IN VARIOUS SOLVENTS

Solvent	$[\eta]$	k'
Chloroform	1.75	0.34
Benzene	1.12	0.35
Acetone	1.08	0.38

two, presumably a result of differences in solvent–solute interaction, Huggins' characteristic constant, k' (14), is almost unchanged.

Osmotic Pressures with Different Membranes

As previously stated, Robertson, McIntosh, and Grummitt (32) found that, for polyvinyl acetate in acetone, swollen cellophane membranes prepared by the method of Carter and Record (6) gave a different π/C versus C curve from that obtained when the membrane was treated with sodium hydroxide. This was explained as due to adsorption of polymer on the Carter and Record membranes. Since the dynamic osmometer of Robertson, McIntosh, and Grummitt was not sufficiently accurate to permit the point to be decided definitely, it was reinvestigated for Gelva V 45 in acetone, using the metal-gasketed osmometer. For the Carter–Record membranes, determinations were made on successive fillings until the osmotic pressure became constant. The results are shown in Table III and Fig. 6.

Robertson, McIntosh, and Grummitt (32) state that no appreciable adsorption takes place on membranes that have been treated with caustic.

TABLE III

OSMOTIC PRESSURES OF POLYVINYL ACETATE IN ACETONE WITH DIFFERENT MEMBRANES

Conc., gm./100 cc.	Filling	π (gm./cm.^{2})	$\frac{\pi}{C_2}$	$\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^2} C_2^2$
Carter–Record membranes				
0.414	1	0.830	2.00	
	2	0.940	2.27	
	3	0.994	2.39	
	4	0.970	2.35	2.36
0.628	1	1.659	2.64	
	2	1.699	2.70	
	3	1.705	2.71	2.68
1.01	1	3.36	3.34	
	2	3.37	3.35	
	3	3.37	3.35	3.28
1.22	1	4.50	3.69	
	2	4.55	3.73	
	3	4.61	3.77	3.67
(0.0)		—	1.63	1.67
2% Caustic treated membrane				
0.594	—	1.61	2.71	2.69
0.997	—	3.35	3.36	3.29
0.270	—	0.602	2.23	2.22
0.0	—	—	1.80	1.82

In the present work, at low pressures, sufficient adsorption took place to decrease the osmotic pressure by 2 to 3%. At the higher pressures, at which Robertson *et al.* worked, no adsorption was detected. Since the extent of adsorption was itself not of particular interest for caustic treated membranes, accommodation of the membranes with solution for at least six hours was adopted as standard practice before the final filling was made.

Adsorption by Carter–Record type membranes was higher than for caustic treated membranes. The decrease in osmotic pressure on this account varied from 0.3 to 14.4%. This is less than that observed by Robertson, McIntosh, and Grummitt (32). However, the membranes in the present work were highly swollen, and Robertson (31) notes qualitatively that adsorption effects with fully swollen membranes are less pronounced.

In contrast with the results of Robertson *et al.*, the curve for the caustic treated membrane is above that for the untreated one. However, the present work shows definitely that the intercepts for the two curves are different.

At present it is not possible to state whether the differences between the results of Robertson, McIntosh, and Grummitt and the present work are due

to the nature of the Carter–Record membranes employed in the two cases or whether the effect is due to the improved sealing at the membrane face in the present work.

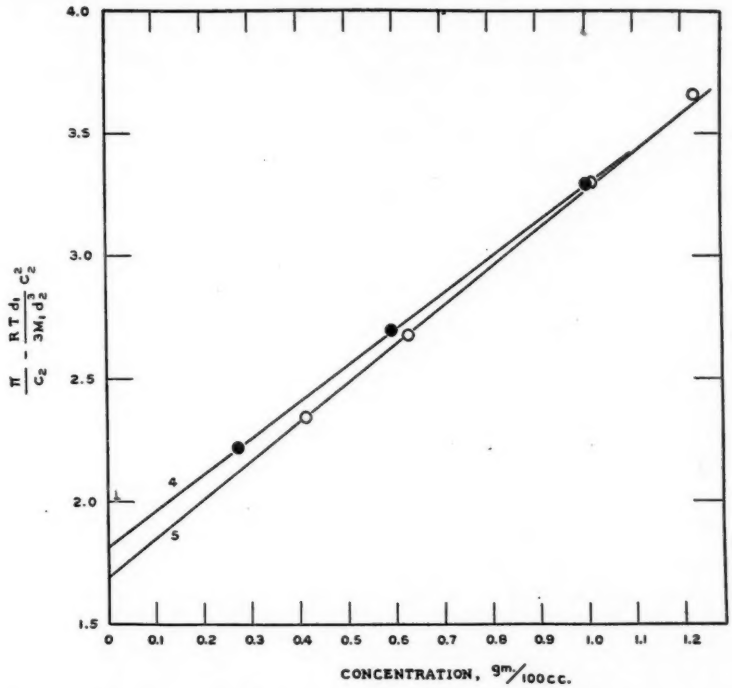

FIG. 6. *Molecular weight of Gelva V 45 with Carter and Record and with caustic treated membranes. 4. Caustic treated membrane. 5. Carter and Record membrane.*

Constancy of Slope

According to Huggins (13), the slopes of the plot π/C_2 versus C_2 or, where significant, $\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3}C_2^2\right)$ versus C_2, should be independent of molecular weight, as also should be the characteristic constant, μ_1, calculated from it. Flory (8) states that μ_1 should be slightly dependent on molecular weight. Plot 7 and Table IV show that, for three samples of polymethyl methacrylate in chloroform with 2% caustic treated membranes, the slopes vary by only 2.8%. The values of μ_1 are likewise constant within experimental error.

DISCUSSION

With an improved type of osmometer, suitable for use with dilute solutions, difficulties due to leakage of solvent through cellophane gaskets and to formation of bubbles within the osmometer have been largely overcome. While

TABLE IV

CONSTANCY OF SLOPE FOR OSMOTIC PRESSURES OF POLYMETHYL METHACRYLATE IN CHLOROFORM

Caustic treated membrane

——	NDR 474	NDR 471	NDR 359
$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^2} C_2^2\right)_{C_2=0}$	0.635	0.415	0.225
Slope	1.62	1.68	1.67
μ_1	0.427	0.424	0.424
$M_n \times 10^5$	4.05	6.19	11.4

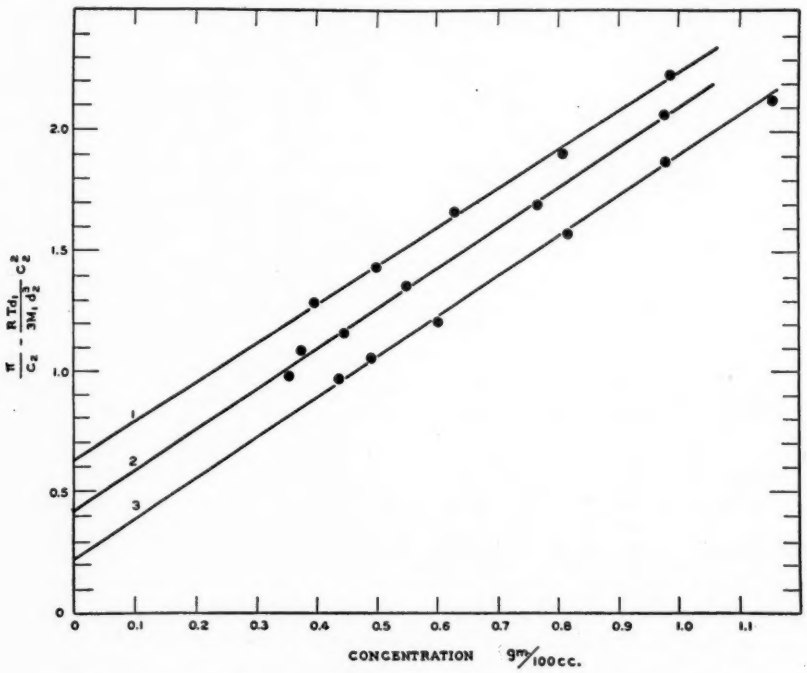

FIG. 7. *Constancy of slope with different molecular weights of polymethyl methacrylate in chloroform. 1. NDR 474. 2. NDR 471. 3. NDR 359.*

it is probable that leakage and bubble formation existed in osmometers used by other workers but were masked by large tubes, it is unlikely, in most cases, that major errors were introduced, since many other workers used corrections to account for finite pressure differences with solvent in both half-cells. Also

many workers used membranes of denitrated collodion of very high permeability, which would tend to decrease the error. Nevertheless, trials with both the old types of osmometer and the improved, metal-gasketed type indicate that the metal-gasketed osmometer gives generally better performance and less scattering of points with cellophane membranes.

The major remaining difficulty lies in the tediousness of the determinations. This is mainly due to the time required to eliminate bubbles. The gold plated osmometer in use at present (22) suffers from this difficulty to a much lesser extent. It is conceivable, also, that what bubbles are formed would be eliminated more readily if the cell were equipped with vertical, rather than concentric, grooves. Determinations can generally be made overnight.

With these difficulties in mind, preliminary measurements have been made with a potentially more convenient type of osmometer involving a membrane of copper ferrocyanide (27) deposited in a disk of sintered glass. Promising results have been obtained, although Murray (28) states that such membranes are not suitable for non-aqueous solutions. One membrane has been shown to be semipermeable to a 3% solution of polyvinyl acetate (molecular weight 140,000) in acetone (22). If workable, this type of membrane would have many advantages in simplifying cell design, elimination of membrane flap, etc., and would provide an additional type of membrane for studying the effect of membranes on the observed osmotic values.

The work of Robertson, McIntosh, and Grummitt (32) on membrane preparation has been largely confirmed and extended to show that cellophane membranes, treated with caustic, yield molecular weights differing from those obtained with untreated membranes. It is noteworthy that the curves determined with caustic treated membranes agree with those determined by Robertson, McIntosh, and Grummitt, while those determined with untreated membranes differ decidedly. The reason for the disagreement is not understood.

Using the metal-gasketed osmometer, it has been shown that, for Gelvá V 45 in various solvents, the osmotically determined molecular weights are identical within experimental error, although the slopes of the $\frac{\pi}{C}$ versus C curves may vary. The viscosity curves, on the other hand, may give widely differing values for the intrinsic viscosity. It is of interest to note that both the osmotic pressure curves in benzene and acetone and the viscosity curves in benzene and acetone are nearly identical, but vary widely in the case of chloroform. That this behaviour is related to the degree of solvent–solute interaction is shown by the difference between the value of μ_1 for chloroform and for the other two solvents. Huggins' characteristic constant, k', however, determined from viscosity measurements, shows little change from solvent to solvent. It must be concluded, therefore, that this constant is too insensitive to be of much value for the systems studied here.

It is noteworthy that Huggins (14) attributes changes with molecular weight in μ_1 of the order of 0.06 to slight chemical differences in the polymers

or to small amounts of impurities. In the present work, the experimental error in μ_1 is estimated from the outside limits of the reproducibility of the osmotic pressure curves as 0.005. It is unlikely, therefore, that Huggins' change of 0.06 can be attributed to experimental error. However, in the present work, for polymethyl methacrylate in chloroform (instead of acetone) no appreciable change of μ_1 with molecular weight has been observed.

Part II

Instability of Solid Polymers

Experimental

In order to eliminate solvation effects on ageing, the changes which take place in solid polyvinyl acetate and polymethyl methacrylate over long periods of time were investigated both in the presence and in the absence of oxygen. For each series a set of three glass bombs of 500 cc. capacity was prepared, each containing 10 to 50 gm. of dry polymer. Samples that were to be aged in vacuum were pumped to a vacuum of 10^{-4} mm., flushed with carbon dioxide, again pumped to 10^{-4} mm. and sealed off. Those to be aged in oxygen were evacuated, flushed with oxygen, re-evacuated, filled with oxygen to a pressure of $\frac{1}{2}$ atm. and sealed off. All bombs were placed in an air-bath at $100 \pm 1°$ C.

Bombs from the various sets were removed periodically, opened, and their contents investigated. In cases where the polymer had fused to the bomb, it was necessary to dissolve out the complete sample, of known weight, in a known quantity of solvent. Aliquots were taken as necessary for investigation. Small quantities of moisture were absorbed during solution and on standing. Consequently the solvent was pumped off the aliquots at room temperature, and the residue taken up with known quantities of dry solvent.

Viscometric and osmotic data were determined as previously described. In addition, in order to investigate any chemical changes during ageing, saponification values were determined on samples of aged polyvinyl acetate by the method of Minsk *et al.* (24).

Results

While polymethyl methacrylate retained its initial whiteness throughout the ageing experiments, the polyvinyl acetate changed in colour from white to pale yellow, the colour deepening with time and being more intense in the polymer aged in oxygen. The Gelva V 15, on account of its low molecular weight, fused to a clear, glassy mass, which underwent the usual colour changes.

Viscosities of aged polymethyl methacrylate were determined both in benzene and in chloroform, while those of polyvinyl acetate were determined in acetone. For each sample, from a plot of $\frac{\ln \eta_r}{C}$ versus C, extrapolated to infinite dilution, the intrinsic viscosity $[\eta]$ and the Huggins, characteristic constant, k', (12), were determined.

Table V summarizes the viscosity data for the polymers studied.

TABLE V

AGEING OF POLYMERS

—			Unaged	In vacuum 2 weeks	In vacuum 3 months	In vacuum 4½ months	In vacuum 6½ months	In oxygen 2 weeks	In oxygen 3 months	In oxygen 4½ months	In oxygen 6½ months
Polymethyl methacrylate											
NDR 359	Benzene	$[\eta]$	7.96	7.47	7.52	7.55	7.41	7.26	6.86	6.50	6.42
		k'	0.40	0.41	0.41	0.40	0.40	0.39	0.39	0.37	0.37
	Chloroform	$[\eta]$	10.06	9.76	9.59	9.59	9.48	9.19	8.53	8.65	8.13
		k'	0.40	0.40	0.40	0.40	0.40	0.39	0.40	0.38	0.40
NDR 471	Benzene	$[\eta]$	4.28	4.29	4.37	4.28	4.16	4.24	4.09	3.82	3.95
		k'	0.38	0.38	0.38	0.37	0.38	0.37	0.36	0.35	0.35
	Chloroform	$[\eta]$	5.62	5.59	5.58	5.55	5.39	5.56	5.16	5.04	4.93
		k'	0.38	0.38	0.37	0.38	0.39	0.38	0.38	0.37	0.39
NDR 474	Benzene	$[\eta]$	3.58	3.69	3.65	3.54	3.68	3.43	3.47	3.28	3.27
		k'	0.36	0.39	0.35	0.35	0.36	0.36	0.35	0.35	0.35
	Chloroform	$[\eta]$	4.80	4.84	4.55	4.55	4.72	4.66	4.45	4.17	4.22
		k'	0.37	0.37	0.37	0.38	0.37	0.37	0.36	0.37	0.38

—		Unaged	In vacuum 24 days	In vacuum 44 days	In vacuum 71 days	In vacuum 76 days	In vacuum 118 days	In oxygen 24 days	In oxygen 51 days	In oxygen 111 days	In oxygen 123 days
Polyvinyl acetate in acetone											
Gelva V 15	$[\eta]$	0.636	0.639	—	0.644	—	—	—	0.621	0.596	—
	k'	0.35	0.35	—	0.35	—	—	—	0.34	0.36	—
Gelva V 360	$[\eta]$	2.29	—	2.09	—	2.06	2.09	1.59	—	—	1.50
	k'	0.37	—	0.38	—	0.37	0.37	0.38	—	—	0.38

For all polymethyl methacrylates in vacuum there is a small decrease in viscosity. For polymethyl methacrylates in oxygen there is an initial rapid decrease in viscosity after which only a slow decrease takes place. The viscosity changes for Gelva V 360 follow the same trend as the polymethyl methacrylates, although the initial decrease in viscosity for polymer aged in oxygen is much sharper. In the case of Gelva V 15, the change in vacuum appears to be within experimental error. In oxygen the viscosity decreases as usual. On account of the fusion of Gelva V 15, access of oxygen to the polymer was probably very limited. As a result, the viscosity change for polymer aged in oxygen is quite small.

Osmotic Pressures

To supplement viscosity data, osmotic pressures were determined on representative samples of polymethyl methacrylate (NDR 359) in chloroform and polyvinyl acetate (Gelva V 360) in acetone. The results are shown in Table VI.

TABLE VI

OSMOTIC PRESSURES OF AGED POLYMERS

—	Unaged	In vacuum 195 days	In oxygen 15 days	In oxygen 90 days	In oxygen 195 days
Polymethyl methacrylate in chloroform					
$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^2} C_2^2\right)_{c_2=0}$	0.22	0.22	0.33	0.33	0.33
Molecular weight	1.1×10^6	1.1×10^6	7.6×10^5	7.6×10^5	7.6×10^5
μ_1	0.424	0.424	0.424	0.424	0.424
$[\eta]$	10.1	9.48	9.19	8.53	8.13

—	Unaged	In vacuum 118 days	In oxygen 24 days	In oxygen 157 days
Polyvinyl acetate in acetone				
$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^2} C_2^2\right)_{c_2=0}$	0.74	0.74	1.15	1.22
Molecular weight	3.46×10^5	3.46×10^5	2.20×10^5	2.10×10^5
μ_1	0.440	0.440	0.444	0.443
$[\eta]$	2.29	2.09	1.59	1.42

Although the polymers, when aged in vacuum, changed in viscosity, no corresponding change in osmotic pressure was observed for the two samples tested. In the case of polymers aged in oxygen, the course of the changes in

osmotic pressure versus ageing time are very similar to the course for intrinsic viscosity. There is a sharp initial rise in osmotic pressure, after which the osmotic pressure becomes approximately constant. The values of μ_1 show no appreciable change.

Saponification Values

Although any chain scission which took place probably involved a chemical split, no change in saponification value was noted. This is not surprising since the extent of breakage was of the order of one link in 4000.

Discussion

Dispersion in a solvent is not a necessary step for the degradation of polymers. Furthermore, the magnitude of the changes in solid polymers is, in many cases, of the same order as for those aged in solution (21). As expected, further, from the observations of several workers (21, 26) the changes in oxygen were much greater than for polymer aged in vacuum. Morrison, Holmes, and McIntosh (26) have shown that oxygen is used up during the ageing process.

The slowing down of viscosity changes in oxygen after the initial decrease, however, was not due to lack of oxygen, since the addition of further oxygen had little effect. Naunton (29) found that rubber photogels in excess oxygen degrade to a limiting viscosity value. Osmotic pressure determinations by McIntosh and Morrison (21) on samples aged in oxygen showed that the viscosity changes were accompanied by molecular scission. The course of the ageing process can therefore be explained by the presence, at certain points along the chain, of bonds that are weaker than normal and that chain splitting takes place predominantly at these points. This suggestion is in contrast to the assumption of Kuhn (17) that all bonds are of equal strength, in the case of cellulose derivatives, but is supported by Jellineck (15). McDowell and Kenyon (20) suggest that, in the case of polyvinyl acetate, a weak link results from the entry into the polymer chain of oxygen atoms from the peroxide catalyst or acetaldehyde from the vinyl acetate as a chain ending mechanism. This suggestion is in accord with the fact that the rate of degradation of Gelva V 360 becomes very slow when the molecular weight has decreased to roughly half. This indicates only one weak link per molecule as would be the case if the weak link arose out of the chain ending mechanism. The weak links may also represent small amounts of unsaturation in the chains (34), or occasional trisubstituted carbon atoms.

Although, for all polymers aged in vacuum, a small change of intrinsic viscosity occurred, no corresponding change in osmotic molecular weight was noted. In the case of Gelva V 360 aged in oxygen for 157 days, a change of 38% in viscosity corresponds to a change of 82% in osmotic pressure. Yet for the polymer aged in vacuum, the viscosity change of 9% produces no observable change in osmotic pressure. Similarly, for polymethyl methacrylate in oxygen for 15 days, a change in viscosity of 9% corresponds to a

change in osmotic pressure of 44%. Yet, in vacuum, a viscosity change of 6% leaves the osmotic pressure unchanged. Furthermore, after the initial decrease in molecular weight of polymethyl methacrylate in oxygen, the osmotic pressure remains constant in spite of a further viscosity drop of 12%. McIntosh and Morrison (21) report that the addition of small amounts of ferric chloride to solutions of polyvinyl acetate in bis(2-chloroethyl) ether causes an immediate increase in intrinsic viscosity with no corresponding change in osmotic pressure.

In this connection, it should be noted that the molecular weight of Gelva V 45 in various solvents has been shown to be constant within 1.5%. This is evidence that the experimental error in the determinations of osmotic pressure is less than 1.5% for this range of molecular weight. For the higher molecular weight Gelva V 360, the experimental error would be 3.7% and for polymethyl methacrylate 12%. However, where no change in osmotic pressure took place (Table VI), the agreement is evidently better than that indicated by the estimated errors. In any case, however, the magnitude of the osmotic pressure changes which would correspond to the viscosity changes is greater than the estimated experimental error. In view, however, of the uncertainty still remaining concerning membrane behaviour, there is some possibility that the effect is not a real one.

Present evidence, nevertheless, suggests that viscosity changes may occur without corresponding changes in molecular weight, possibly as a result of the presence of two independent processes. A similar phenomenon has been reported by Alfrey, Bartovics, and Mark (1) whose samples of polystyrene, prepared at various temperatures, had different viscosities, but similar osmotic molecular weights. The viscosity changes without molecular weight changes could be attributed to alterations in the geometrical configuration of the molecules. Mead and Fuoss (23), for instance, in order to explain viscosity effects, suggest that polymer molecules slowly break up, untangle, and elongate. However, in the present work, the fact that the values of μ_1 for polymers aged in vacuum have not changed is evidence that any changes in shape or degree of solvent–solute interaction which took place were small.

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THE POLAROGRAPHIC DETERMINATION OF TIN IN HIGH PURITY ZINC AND ZINC DIE-CASTING ALLOYS[1]

By R. C. Hawkings,[2] D. Simpson,[3] and H. G. Thode[4]

Abstract

A procedure has been developed for the determination of tin in high-purity zinc and zinc die-casting alloys present in amounts from 0.001 to 0.2%. The samples are dissolved in sulphuric acid, oxidized with hydrogen peroxide, precipitated with cupferron, redissolved and reduced, and finally the tin is determined polarographically. By this method, the tin can be determined with an accuracy of ± 2.0% when present in amounts less than 0.005%. A method is now available for the routine polarographic determination of trace amounts of copper, lead, cadmium, and tin in high-purity zinc and zinc die-casting alloys with a high degree of accuracy and precision.

Introduction

The discovery that trace amounts of lead, cadmium, and tin cause intergranular corrosion in zinc die-casting alloys, which results in a serious weakening of the alloy, makes it important to have available a rapid and accurate method for determining trace amounts of these elements. The spectroscopic method has been applied with a fair degree of success, but the equipment necessary is expensive. Several years ago Hawkings and Thode (2) reported a procedure for the routine polarographic determination of trace amounts of copper, lead, and cadmium. A procedure for the polarographic determination of tin was also developed to complete the group of elements mentioned above. However, publication of the latter procedure has been held up because of security regulations. This paper deals with the determination of trace amounts of tin in the presence of zinc and other metals, and describes a polarographic procedure that has been used successfully for several years.

Smrž (10) made a study of stannous tin and found that in a chloride solution (0.5 to 0.1 *N* hydrochloric acid) the wave for tin almost coincides with that of lead, and that it was possible to determine tin to 10^{-6} mole per litre, provided the stannous solutions were fresh, free from oxygen, and acidic. He also observed an ageing effect for stannous tin in alkaline solutions, which made the quantitative determination of tin in such a medium difficult. Kalousek (3) studied the redox system of tin and found that stannic chloride is not reducible except in very strong chloride solutions (above 0.1 *N*) where its reduction appears inhibited. He also observed waves for stannous tin in alkali and citrate solutions. Strubl (11) investigated the anodic oxidation of the stannous tartrate complex. Lingane and Scott (5) were able to obtain

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waves for stannous tin in 2 *N* perchloric acid and for stannic tin in 2 *N* perchloric acid in the presence of at least 0.5 *N* chloride. Shakhov (9) determined stannous tin in potassium fluocolumbate and metallic columbium (niobium), using an alkaline citrate medium. Winkel and Proske (12) state that in acid and neutral solution, cobalt, lead, and tin (ous) come too close together to give separate waves. In alkaline solutions a good separation is obtained. Cozzi (1) determined tin in white metals by difference from the sum of the lead and tin (ous) waves. The lead alone was determined in alkali medium, and the sum of tin and lead by reduction in acid chloride medium. Seith and Esche (8) also used the method of measurement of difference for tin in zinc. The lead wave alone is obtained by volatilizing the tin as stannic chloride from acid solution.

The work of the above authors indicates that the applications of the polarograph to the determination of tin are nearly always complicated by the fact that the tin (ous) wave is almost coincident with that of lead. The determination of tin by difference is inclined to be inaccurate when the lead concentration exceeds that of the tin by a factor of approximately five. Cozzi (1) partially surmounted this difficulty by making a preliminary separation of most of the lead, but this particular procedure is rather impractical for trace elements in zinc owing to the difficulties of precipitation. The purpose of this investigation was, therefore, to develop an accurate method for the determination of trace amounts of tin (0.001% or less) in high purity zinc die-casting alloys by as direct a method as possible.

Cupferron has been successfully used as a precipitant for the separation of tin from many metals. Attempts to separate tin from lead in zinc alloys met with rapid success and resulted in the present successful method. Lundell and Knowles (7) have surveyed the uses of cupferron as a reagent in quantitative analysis, but make no mention of the determination of tin. The most complete survey of the uses of cupferron in quantitative analysis is presented by Lundell and Hoffman (6), who list in a table the effect of cupferron on the elements of the periodic system when used in 1 : 9 sulphuric or hydrochloric acid. According to this table, cupferron can be used to separate tin and lead in the presence of zinc, magnesium, and aluminium, found in zinc die-casting alloys. However, no mention has been made of the use of cupferron for the separation of micro quantities of tin, of the order of 10^{-2}%, particularly in the presence of a large excess of other metal ions such as are found in zinc and zinc die-casting alloys.

Apparatus and Reagents

This work was carried out exclusively with the Heyrovsky Model XI Polarograph (E. H. Sargent and Co.) which has a galvanometer sensitivity of 0.0027μ amp. per mm. The same capillary was used as in the work on copper and lead, and cadmium, and the precautions observed were the same. The electrolysis cell with an external anode was of a design similar to that of Lingane and Laitinen (4) (Fig. 1). The solution of the samples was carried

out in 150 ml. beakers which were cooled in a bath of running water prior to precipitation. Filtrations were made with Jena No. 3 sintered glass crucibles, and the precipitate was dissolved in the apparatus shown in Fig. 2. Reductions were carried out in a 50 ml. flask, through which a steady stream of carbon dioxide was passing. After reduction, the flask was cooled to 25° C. and finally after proper dilution a portion of the solution was transferred to the electrolysis cell as shown in the diagram (Fig. 1). A stream of carbon dioxide

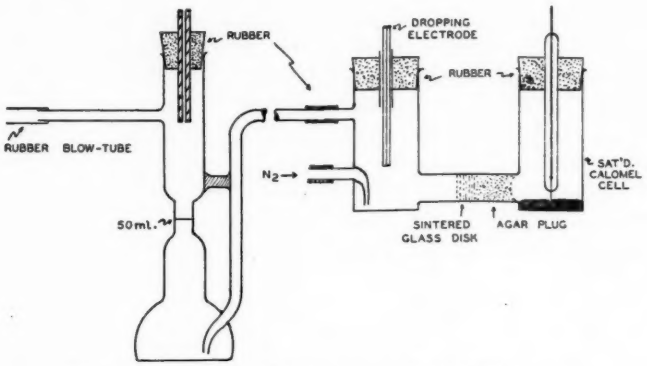

FIG. 1. *Electrolysis cell showing transfer of reduced solution.*

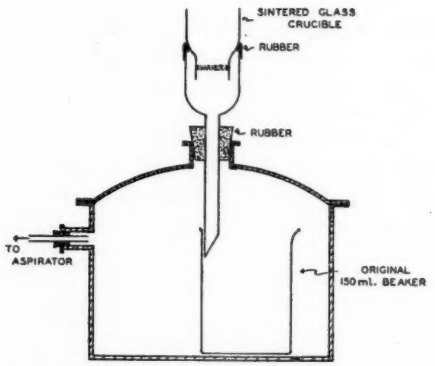

FIG. 2. *Apparatus for solution of precipitate.*

or nitrogen was maintained through the solution in the electrolysis cell during the transfer, and over the solution when measurements are being made.

The reagents outlined were tested for tin content by the method of difference. After proper treatment, the residue in each case was added to 10 gm. of analysed zinc, and the whole carried through the procedure for tin. After subtracting the residual current for the tin in the zinc and reagents, the correction for the tin in the reagent tested was obtained. The over-all effect

of tin impurities in the reagents used amounted to 0.00011%, which would have to be subtracted from the percentage of tin found in the zinc sample.

Procedure

To 10 gm. of zinc in a 150 ml. Pyrex beaker add 50 ml. of distilled water and 15 ml. of concentrated sulphuric acid (sp. gr., 1.84). When the reaction has subsided, warm on a sand-bath to complete the solution of the zinc. Wash down with distilled water, dilute to 100 ml. and add 5 ml. of 30% hydrogen peroxide. Boil until solution is complete and all hydrogen peroxide is decomposed.* Dilute again to 100 ml., add 5 ml. concentrated hydrochloric acid (sp. gr., 1.19) and cool in running water (15° C. or less).† Add about 3 ml. of a 5% solution of cupferron (stabilized with phenacetin‡) drop by drop with constant stirring. Stir until the precipitate coagulates.§ Stir in approximately 0.1 gm. of Analytical Filter-Aid (Johns–Manville Co.) and filter within half an hour (keep solution cool if allowed to stand with precipitate) using moderate suction on a Jena No. 3 sintered glass filtering crucible. Wash beaker and precipitate with 20 ml. of 0.05% cupferron solution, containing the 1 : 50 sulphuric acid. Dissolve precipitate in the filtering crucible with 10 ml. concentrated nitric acid (used in small portions, e.g., 5 + 5 or 3 + 3 + 4) and wash with water, collecting the filtrate in the original beaker. Add 4 ml. concentrated sulphuric acid and evaporate to fumes. Cool, add 5 ml. nitric acid and evaporate again to fumes. Wash down with 10 ml. of water and warm to dissolve salts. Transfer to a 50 ml. reduction flask, using a rubber policeman to ensure complete transfer. Add 4 ml. concentrated hydrochloric acid and 0.1 gm. pure aluminum foil. Heat gently in a stream of carbon dioxide until clear and then for 15 to 30 min. longer to ensure complete solution of the tin. Cool, add 1.25 ml. of fresh 0.1% gelatin solution and dilute to volume with freshly boiled distilled water. Cool to 25° C., adjust volume, transfer to electrolysis cell, through which a stream of nitrogen is passing, and electrolyse immediately from − 0.3 to − 0.7 v., using a saturated calomel reference electrode. Record polarogram at greatest sensitivity possible.

Results and Discussion

The electrocapillary curve and capillary constant in the medium in which the tin is determined were measured for the purpose of referring results to other capillaries. The temperature of measurement was 25.0° C. and h = 36.5 cm. of mercury.

* *If solution is not complete add a second portion of hydrogen peroxide. The absence of hydrogen peroxide is indicated by the absence of small bubbles at the surface of the boiling solution. Add extra water if necessary to keep salts in solution.*

† *Cf. section on interference of lead.*

‡ *5% Cupferron (5 gm. B.D.H. cupferron; 0.25 mgm. acetophenetidine (phenacetin)). Dilute to 100 ml.*

§ *Sometimes, in the presence of certain quantities of elements such as lead, arsenic, antimony, or, for unknown reasons, the precipitate will not coagulate. In such an event, filter after 10 min. stirring.*

TABLE I

ELECTROCAPILLARY CURVE

Potential, v.	0 (Cell disconnected)	0 (Cell connected)	−0.3	−0.5	−0.7
Time (25 drops), sec.	78.75, 81.40, 79.60	80.10, 80.30	80.6, 80.5	84.1, 84.3	84.15, 84.25
Drop time, sec.	3.20	3.21	3.22	3.36	3.36

TABLE II

CAPILLARY CONSTANT

Applied potential	Temp., ° C.	No. drops	Time, sec.	Weight, mgm.	$m^{2/3}t^{1/6}$
−0.5	24.8	50	168.4	211.7	1.43
−0.5	24.8	50	169.2	213.7	1.43

The capillary was next calibrated for tin by making additions of tin from the diluted stock solution. The calibrations were carried out over a concentration range of 10^{-6} M to 3×10^{-3} M and the step-heights obtained by difference from the residual current of the tin present in the zinc used as a base. The calibration constants for three successive calibrations are given in Table III.

TABLE III

CALIBRATION CONSTANTS FOR TIN IN ZINC

Added conc. Sn, moles/litre	Per cent added Sn (10 gm. Zn in 50 ml.)	(1) Factor %/μamp.	(2) Factor %/μamp.	(3) Factor %/μamp.	Av. Factor %/μamp.
1×10^{-6}	0.0000_6	0.00375	0.01362	0.02500	0.0141
5×10^{-6}	0.0003_0	0.01428	0.01605	0.01356	0.0146
2.5×10^{-5}	0.0014_8	0.01558	0.01586	0.01756	0.0163
1.25×10^{-4}	0.0074_2	0.01418	0.01645	0.01432	0.0148
6.25×10^{-4}	0.0371	0.01322	0.01347	0.01336	0.0134
3.13×10^{-3}	0.1855	—	0.01264	0.01735	0.0151
				Average factor	0.0147

The factors were obtained in terms of per cent of the metal per microampere of diffusion current for a 10 gm. sample of zinc in 50 ml. of solution for the sake of convenience in calculating the results of analyses.

In order to determine the precision of the method, and to discover the greatest source of error in the procedure, four series of determinations were carried out.

(*a*) Precision of repeated determinations on the same cell,

(*b*) Precision of repeated determinations on different aliquots of the same solution,

(*c*) Precision of repeated determinations on different samples of the same alloy,

(*d*) Precision of repeated measurements on same curves for:

(1) Different individuals,

(2) The same individual.

TABLE IV

PRECISION OF POLAROGRAPHIC PROCEDURE

Series	Tin		
	Average %	Average deviation, %	Method
(*a*)	0.0020_9	±0.00004	Average deviation from mean of eight runs.
(*b*)	0.0019_0	±0.00003	Average deviation from mean of five runs in duplicate.
(*c*)	0.0021_0	±0.00008	Average deviation from mean of seven samples (duplicate runs).
(*d*) (1)	0.0007_4	±0.00002	Average deviation from mean of two observations on each of six different curves for nine individuals.
(2)	0.0007_3	±0.00002	Average deviation from mean of 10 observations on each of six different curves by the same individual.

It is apparent that the error of reproduction of the curves by the instrument is very small, and that the error is almost entirely that of measurement of curve heights in this case. The error of repeated determinations on different samples is of the same order as the error of measurement of curve heights.

The accuracy of the procedure was determined by the analysis of a series of samples from the National Bureau of Standards, Washington, D.C. The results are shown in Table V.

TABLE V

ACCURACY OF METHOD

EXPERIMENTAL VALUES

(% Sn per 10 gm. of Zn in 50 ml.)

Sample No.	(1)	(2)	Av.	Corrected value	Certificate value
No. 108 spelter	0.0008_3	0.0007_1	0.0007_7	0.0007 ± 0.0001	0.0008
No. 109 spelter	0.0004_2	0.0004_3	0.0004_3	0.0003 ± 0.0001	0.0002
No. 110 spelter	0.0005_4	0.0005_7	0.0005_6	0.0005 ± 0.0001	0.0005
No. 94 Al, Mg, Cu, die-casting alloy	0.0007_2	0.0009_2	0.0008_2	0.0007 ± 0.0001	<0.0005

Table V indicates that within the limit of the precision, the method is accurate to $1 \times 10^{-4}\%$ except in the case of the die-casting alloy, where the error is $2 \times 10^{-4}\%$. No explanation is available for the greater error in this case.

Aluminium Reduction

The reduction process used in the procedure for tin was developed in our own laboratory for the purpose on hand, and, as a result, a few essential facts about its manipulation will be given. The process is based upon the fact that metallic aluminium reduces tin to the metallic state quantitatively, and the resulting tin redissolves hydrochloric acid to the stannous state in an inert atmosphere.

Experiments have indicated that from 1 to 10 ml. of concentrated hydrochloric acid is quite satisfactory for amounts of tin up to 0.002%, but 4 to 5 ml. is recommended as ideal, in that the process is neither too slow nor rapid enough to be violent. In the event that the tin content is in excess of 0.007%, an increase in the amount of hydrochloric acid added is advisable. Add 6 ml. hydrochloric acid when tin content is 0.04% and 8 ml. hydrochloric acid when tin content is 0.2%. By this means, the reduction proceeds in a reasonable length of time. Additions of aluminium-foil from 0.025 to 0.05 gm. were tried and were equally successful in the presence of 0.002% tin but 0.5 gm. of aluminium caused a violent action. Aluminium of approximately 0.1 gm. is recommended. Studies of the time of digestion after the solution has lost its turbid appearance indicate that from 15 to 30 min. is the best.

With these refinements, the procedure is satisfactory for tin concentrations up to 0.2%. It should be feasible to use higher concentrations, although this has not been investigated. In such a case, a smaller sample would be preferable.

Interfering Elements

The interference of some 19 elements that may be found in zinc, either as alloying elements, or as impurities, has been considered. They are listed as follows: Sn, Sb, As, Pb, Bi, Cu, Cd, Fe, Ni, Co, Mn, Tl, In, Ag, Hg, Ge, Ga, Al, and Mg.

Of these, tin is to be determined. According to Lundell and Hoffman (6), cupferron in diluted 1 : 9 hydrochloric or sulphuric acid will precipitate Sn, Sb, Bi, Ge, Fe, completely, Cu and Tl incompletely. Furthermore, no precipitation of Sb as Sb^{+++++} will occur. This leaves only Bi, Ga, Fe, Cu, and Tl as possible interfering elements. In a reduced chloride medium Ga and Fe^{++} would not be expected to interfere because their discharge potentials are above that of Sn^{++}. This leaves only Bi, Cu, and Tl as interfering elements from a polarographic point of view, and two of these, Cu and Tl, are known to be incompletely precipitated.

Extensive experiments have shown that there is absolutely no interference from Co, Hg, Mn, Ni, Ag, Fe, Tl, Sb, when these elements are present in amounts of 0.05%. In every case this is more than would normally be

expected in high purity zinc or zinc die-casting alloys. The Fe may possibly be an exception to this, but as pointed out above, the Fe^{++} has a discharge potential well above that of Sn^{++}. Cd up to 1% has no detectable effect on the determination of Sn. Bi was tried at the level of 0.05%, and although a black residue appeared in the reduction flask (Bi), the wave for tin was quite normal. Al and Mg were already present in the metal used for the development work in amounts of approximately 4% and 0.1%, respectively. That there is no interference from these elements is borne out by the fact that the calibrations for Sn were made in their presence and the procedure applied with equal success to spelters (cf. B. Stds. No. 108, No. 109, No. 110). In, Ge, and Ga were not tried partially because of the difficulty of procuring the respective salts and partially on the basis of the confirmation of Lundell and Hoffman's work, on elements precipitated by cupferron by the writers. Of the other three, only one, Ga, is expected to precipitate and this has a higher discharge potential than Sn. Arsenic is not expected to precipitate and tests with 0.05% arsenic show no interference from this source.

The two remaining elements, Pb and Cu, were found to give difficulty. The Pb is not precipitated by the cupferron, but is separated with the cupferron precipitate of Sn as lead sulphate which later dissolves in the nitric acid to appear as Pb^{++} in the final solution. Cu is incompletely precipitated and appears in the final solution in the extent to which it is precipitated.

It was found, however, by the addition of 5 ml. concentrated hydrochloric acid to the solution prior to cupferron precipitation, that Pb up to 0.01% can be present without precipitation of lead sulphate. For the determination of Sn in the presence of larger amounts of Pb (up to 1.3% tried) the Pb can be removed by suction filtration on a sintered glass crucible of the oxidized sulphuric acid solution to remove lead sulphate, followed by the addition of 5 ml. hydrochloric acid and the precipitation of the Sn with cupferron. The use of larger amounts of hydrochloric acid is not sufficiently effective to warrant its use.

The interference of Cu presented a more difficult problem. Copper up to 0.04% can be tolerated by the procedure, and even amounts of 0.25% are not impossible, although in this extreme case the limit of detection drops because of the necessity for using a lower galvanometer sensitivity to compensate for the Cu. It was found, however, that by a rapid 30 min. deposition of the Cu from the sulphuric acid solution using 2 amp. at 5 v. and a rotating gauze anode, that 3% of Cu can be removed to such an extent that no interference is found. Experiments indicate Cu from 0.05% to 3% are easily deposited. The deposition is practically quantitative, giving slightly high results for copper, owing to contamination of the deposit. The deposition is not affected by the presence of as much as 0.2% tin which is quantitatively determined in the electrolyte by the usual procedure. Deposition times from 15 to 60 min. were tried and deposition was found to be sufficiently complete in 30 min. for the purpose on hand.

The procedure developed for the polarographic determination of tin in high purity zinc and zinc die-casting alloys is accurate and precise in the presence of 19 elements, which are liable to be present in varying amounts for tin contents ranging from 0.001 to 0.2%. Furthermore, because of the nature of the procedure, it has applications, with suitable modifications, for the microdetermination of tin in numerous other materials without recalibration of the capillary.

It should also be pointed out that although the procedure for tin was developed using a 10 gm. sample of zinc, there is no reason why a larger or smaller sample could not be used. If, for example, a 100 gm. sample is used, it should be possible to detect $1 \times 10^{-5}\%$ of tin following the procedure (with suitable modifications).

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Concerning the Theoretical Aspects of the Reaction of Cyanogen and 1,3-Butadiene

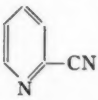
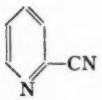
In an earlier communication the reaction of cyanogen with 1,3-butadiene was discussed, and the formation of the product, α-cyanopyridine, was formulated as a Diels–Alder type of reaction in which cyanogen had the role of dienophile (3). This note concerns the thermodynamic considerations of this reaction, and a correlation of these calculations with the experimental results. The thermodynamic approach is of interest and importance in that it enables a schematic picture to be formed of the feasibility of the reactions at various temperatures.

For the present calculations most of the data required were obtainable from those reported in the literature. For butadiene, the heat of formation, 26.748 kcal. (6), the entropy 66.42 cal. deg.$^{-1}$ (12), and the heat capacity equation $C_p^0 = 3.348 + 5.479 \times 10^{-2}\ T - 18.21 \times 10^{-6}\ T^2$ (9) were used. For cyanogen, the heat of formation 71.8_2 kcal. (2) for carbon as graphite, the entropy 57.64 cal. deg.$^{-1}$ (7) and the heat capacity $C_p^0 = 9.982 + 14.48_4 \times 10^{-3}\ T - 6.207 \times 10^{-6}\ T^2$ (8) were used. For α-cyanopyridine the heat of formation, 62 kcal., was calculated from bond energies and resonance energy, the entropy 77.09 cal. deg.$^{-1}$ and the heat capacity equation $C_p^0 = 14.81_5 + 5.807 \times 10^{-2}\ T - 19.48 \times 10^{-6}\ T^2$ were calculated using the methods of statistical thermodynamics (10, 11) and an assignment of the fundamental vibrational frequencies that was made using the assignment for pyridine reported recently by Kline and Turkevich (5) as a guide. The data for carbon, hydrogen, and nitrogen were taken from Kelley's compilation (4). Using the well known relations between the free energy change, the equilibrium constant, the heat of reaction, and entropy change for a chemical reaction, the values listed in the following table were calculated from these data.

It is a general thermodynamic rule that the free energy change must be favourable for a reaction to be feasible, or that if $\log K_p \geq 1$, the reaction may be considered as a possible one. In the table above it is seen that, from the values of $\log K_p$, both the synthesis and decomposition of α-cyanopyridine are possible in this temperature range. The low yields of α-cyanopyridine, therefore, which were experimentally observed, are very likely due to the fact that there is a considerable pyrolysis of the product occurring at the temperature of the reaction.

A similar calculation was made for the formation of 1,4-dicyanobutene-2 from cyanogen and butadiene, using the methods and tables of Anderson, Beyer, and Watson (1) to approximate the necessary thermodynamic data. The prediction for this reaction is that it also is a feasible one over the temperature range considered above. However, none of this product was observed in the work reported concerning the reaction of cyanogen and butadiene (3). A possible reason for this is that the 1,4-dicyanobutene-2, lacking the stability against pyrolysis conferred to the α-cyanopyridine by the resonance in the pyridyl nucleus, does not survive the experimental conditions.

VALUES OF LOG K_p IN THE RANGE 300° TO 1200° K FOR THE SYNTHESIS AND DECOMPOSITION OF α-CYANOPYRIDINE

Reaction	(° K) T =	300	400	500	600	700
$CH_2{=}CH{-}CH{=}CH_2 + (CN)_2$ =	log K_p =	23.1	16.5	12.6	10.0	8.2
(1)  $+ H_2$						
Reaction	T =	800	900	1000	1200	
(1)	log K_p =	6.8	5.7	5.0	3.7	
Reaction	(° K) T =	500	600	700	800	
(2)  $= 6C + 2H_2 + N_2$	log K_p =	35.9	31.6	28.4	26.1	
Reaction	T =	900	1000	1200		
(2)	log K_p =	24.3	22.8	21.0		

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